THE MECHANISM OF GAS ABSORPTION ON FRESHLY FORMED LIQUID SURFACES.

by

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SUMMARY

The work presented by the author is intended to prove or disprove the validity of the theories of the mechanism of gas absorption, and, if need be, extend or develop a new theory. There are four main theories which can be divided into two classes (a) the "two film" and (b) the "penetration" hypotheses.

The introduction to the work describes each of the four theories in detail. Also contained in the introduction is a survey of previous experimental data as related to the existing theories.

In Section I of the experimental work the absorption characteristics of a high speed rotary absorber, working on five solute gas systems, viz., ammonia, methanol, methyl acetate, acetone and carbon dioxide (all in water) are discussed in relation to the absorption mechanism. The evidence does not favour any one of the theories in particular, but the absorption effects have been masked by almost complete removal of the very soluble gases included in the programme,

A smaller absorber giving less complete absorption, was constructed and the results obtained from two systems/

systems, ammonia-air-water and carbon dioxide-air-water, are discussed in Section II.

In an attempt to establish a clearer picture of the absorption mechanism in these absorbers and to test more directly the application of the existing theories experiments were carried out on absorption - desorption at a liquid jet. The description of the apparatus and discussion of results appears in Section III. There was some indication that the penetration theory could, if suitably modified, explain the mechanism of mass transfer. To give further proof of this theory (Section IV) a high speed absorption technique was developed. It was unfortunate that certain drawbacks in the design of the apparatus prevented conclusive evidence, in favour of the modified theory, to be given.

Finally a modified penetration theory is presented on a mathematical basis and the experimental data reviewed in the light of this modification (Section V).

PUBLICATIONS

The following paper has been published in the Transactions of the Institute of Chemical Engineers, 34, 195, (1956) ,

"Performance Characteristics of a Centrifugal Gas Absorber"

by I.J. RAE and F. RUMFORD.

Another paper entitled,

"Absorption and Desorption at Liquid Jets - Application of the Penetration Theory"

by I.J. RAE, L.J. CRANE and F. RUMFORD.

has been submitted for publication in Chemical Engineering Science.

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INTRODUCTION

The mechanism of gas absorption, although the process is one of the more important chemical engineering operations involving mass transfer from one phase to another, has received relatively little attention compared with the abundance of work published on the performance of the various types of absorption equipment. Actually most of the absorption plants in industry today have been designed on the basis of the Whitman "Two Film" theory[1] which was introduced all of 34 years ago, although certain refinements in the original conception have taken place[2,3]. A second theory, one propounded by Higbie[4], treats gas absorption in the light of the "penetration theory" in which a systematic liquid surface renewal is considered rather than two physical films having a finite resistance to mass transfer. This second theory has been modified by Danckwerts[5] in that he suggests that the liquid surface is renewed irregularly rather than systematically. It will be appreciated that both the above theories, viz., the "two film" and the "penetration", consider that at some stage in the mechanism, transfer of the substance takes place by molecular diffusion. Recently, however, Russian workers/

workers[6,7,8,9,10] suggest that gas absorption into turbulent liquids is independent of molecular diffusion and consider the process as wholly controlled by mass flow to the surface, age of the surface, and the degree of neutralisation of the surface.

Certain empirical relationships based on the analogy between heat, mass and momentum transfer (friction) have been suggested. The possibility of these three individual subjects being treated as a simple branch of science becomes increasingly feasible as new theories on turbulent motion are put forward.

The first attempt at correlation was the "analogy" relating heat transfer and momentum transfer derived by Reynolds[11] in 1874. His analogy was based on the equality of the two ratios

$$\frac{\text{Actual heat given up}}{\text{Total heat available}} \quad \text{and}$$

$$\frac{\text{Momentum loss by skin friction}}{\text{Total momentum available}}$$

The following relationship is obtained

$$h = \frac{f \cdot C_p \cdot \rho \cdot U_{av}}{2} \qquad \text{——————(1)}$$

The corresponding equation for mass transfer as derived by/

by Sherwood and Pigford[12] is

$$k_c = \frac{f \cdot U_{av}}{2} \qquad (2)$$

Now for gases, in which $c = p/RT$ this becomes

$$k_G = \frac{k_c}{R \cdot T} = \frac{f \cdot U_{av}}{2 R \cdot T} = \frac{f \cdot \rho \cdot U_{av}}{2 P_T \cdot M_m} \qquad (3)$$

Data on heat and mass transfer show agreement with (3) to within 35% for gases inside pipes but there is an indication of the importance of the Prandtl number $(C_p \cdot \mu / k)$ in heat transfer and the Schmidt number $(\mu / \rho \cdot D_v)$ in mass transfer. This follows the analysis of Prandtl[13] and Taylor[14] who assumed the existance of a laminar layer at the pipe wall and applied the analogy to this layer and the turbulent central stream, considering them as resistances in series to the heat transfer.

Von Karman[13], extending the treatment to mass transfer, derived a form of Eq. (2) based on eddy diffusivity E and eddy viscosity ϵ. When E and ϵ are negligible compared with D_v and μ, then Karman's analysis reduces to

$$k_c = \frac{\rho \cdot D_v}{\mu} \cdot \frac{f \cdot U_{av}}{2} \qquad (4)$$

Colburn/

Colburn[4] derived a similar equation for mass transfer in gases

$$k_c = k_G . R.T = \frac{\frac{1}{2} f . U_{av} . (P_T / P_{BM})}{1 - a_1 + a_2 (\mu / \rho . D_v)} \qquad (5)$$

where $a_1 = \frac{\text{fluid velocity at boundary of laminar layer}}{\text{average stream velocity}}$

On comparison with experimental data Eq. (5) shows poor agreement in the evaporation of organic liquids, but reasonable prediction of results in water evaporation. In order to obtain better agreement between data and theory in heat transfer Chilton and Colburn[16] introduced the Prandtl function $(C_p . \mu / k)^{\frac{2}{3}}$ as the denominator of the Prandtl - Taylor equation, and, for mass transfer correlation, proposed replacing the denominator of (5) by the empirical group $(\mu / \rho . D_v)^{\frac{2}{3}}$. Thus two new functions j_H and j_D were defined

$$j_H = \frac{h}{C_p . \rho . U_{av}} . \left(\frac{C_p . \mu}{k} \right)^{\frac{2}{3}} = \frac{1}{2} f \qquad (6)$$

$$j_D = \frac{k_c . P_{BM}}{U_{av} . P_T} . \left(\frac{\mu}{\rho . D_v} \right)^{\frac{2}{3}} = \frac{k_G . P_{BM}}{G_m} . \left(\frac{\mu}{\rho . D_v} \right)^{\frac{2}{3}} = \frac{1}{2} f \qquad (7)$$

These two functions indicate a useful relationship between/

between heat and mass transfer due to the tendency of j_D and j_H to vary correspondingly with $\frac{1}{2}f$ when operating under comparable conditions of flow.

Now Eqs. (2), (4), (5) & (7), have the common form

$$k_c = k_G . R.T = \frac{f . U_{AV}}{2 \varphi_D} \qquad (8)$$

where φ_D is the variable denominator 1.0 in (2), $(\mu/\rho . D_v)$ in (4) $1 - a_1 + a_1 (\mu/\rho . D_v)$ in (5) and $(\mu/\rho . D_v)^{\frac{2}{3}}$ in (7). Other heat transfer equations, particularly those of Von Karman[13], Reichardt[17] and Boelter et al.[18], have been modified to suit mass transfer as follows:

Von Karman, $$\varphi_D = 1 + 5\sqrt{\frac{f}{2}}\left\{\psi - 1 + \log\left[(1+5\psi)/6\right]\right\} \qquad (9)$$

Reichardt, $$\varphi_D = \frac{R_c}{R_v}\left\{1 + a_2 + R_v\sqrt{\frac{f}{2}}\left[2(\psi-1) + 13.5\left(\frac{\psi \log \psi}{\psi - 1} - 1\right)\right]\right\} \qquad (10)$$

Boelter et al., $$\varphi_D = 5R_c\sqrt{\frac{f}{2}}\left[\psi + \log(1+5\psi) + \frac{1}{2}\log\left(\frac{R_e}{60}\sqrt{\frac{f}{2}}\right)\right] \qquad (11)$$

By way of comparison of the important semi-theoretical correlations, Fig. 1 shows the plot of $2k_c/f.U_{AV}$ vs $\mu/\rho . D_v$ since φ_D is some function of the/

the Schmidt number. The experimental points are those of Gilliland who measured the vaporization of nine different liquids on a 1" wetted wall column at R_e = 10,000 with f taken as 0.0081. It is seen that Von Karman's theory is very convincing over the range of data presented by Gilliland[19], the theory predicting the experimental results to within 6 per cent.

Other empirical correlations based on heat transfer and momentum transfer analogies have been evolved but these are too numerous to be summarised within this synopsis of absorption mechanisms, and a return must be made to descriptions of the actual fundamental theories of gas absorption.

These theories will be applied first of all to physical absorption in which the phases do not react.

The first conception of the mechanism is the Whitman "two film" theory[1], in which a picture of the suggested mechanism can be formed by considering a liquid formation (jet, drop, sheet or surface) in which a turbulent interior exists. This turbulence (and consequent eddy diffusion process) is assumed to have a decreasing effect on transfer as the surface is approached until, at the proximity of the surface, transfer is only affected by the/

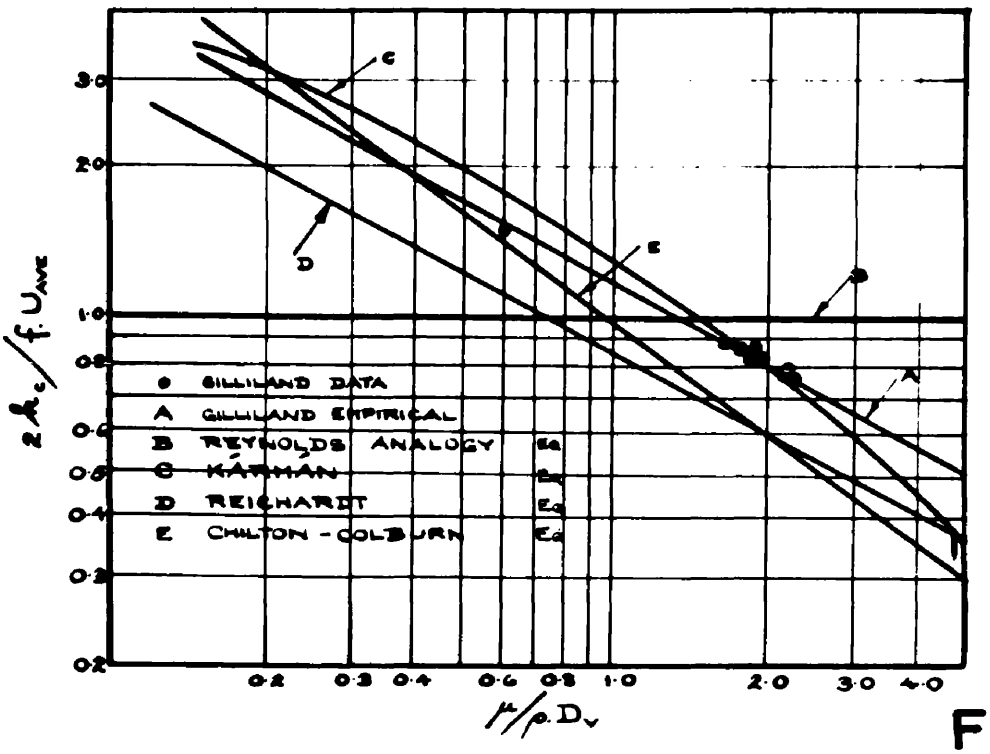


FIG. 1

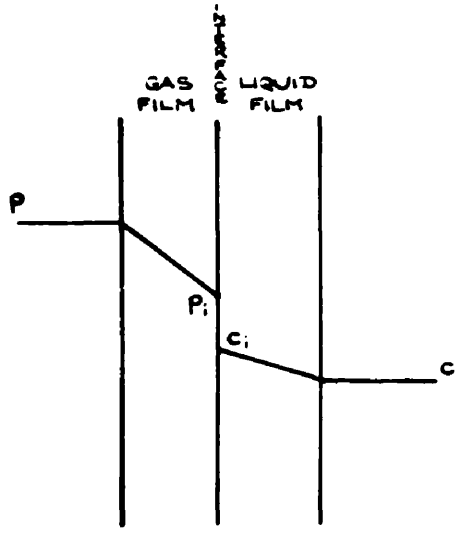


FIG. 2

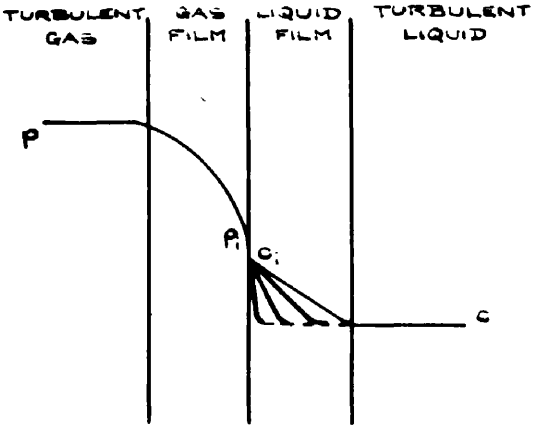


FIG. 3

the relatively slow process of molecular diffusion. The greater the turbulence, the nearer to the actual surface the eddy diffusion extends, thus diminishing the effective resistance region through which transfer takes place by molecular diffusion.

A mathematical analysis of the theory is deduced by considering two films, one gas and the other liquid, on either side of a phase interface (Fig. 2). The resistance to mass transfer at the interface is assumed to be negligible and the two phases are in equilibrium at all points on the surface - the partial pressure of the solute p_i over the solution is governed by c_i the concentration of the solution. Since the effect of eddy diffusion coupled with the molecular diffusion is not known, the unknown diffusivity and the average diffusion path are compounded to give coefficients k_L and k_G defined by (under steady state conditions)

$$N_a = k_L (c_i - c_o) \qquad (12)$$

and for the gas film

$$N_a = k_G (p_o - p_i) \qquad (13)$$

(c_o is the concentration in the body of the liquid; p_o is the partial pressure in the bulk of the gas).

If/

If a more simplified picture[2] is considered then there is a completely stagment film of definite thickness, x_L. This film is assumed to be the only region in which resistance exists and the process of mass transfer in this liquid is assumed to be entirely controlled by the molecular diffusivity of the system which can be established from independent experiments.

Thus

$$N_a = \frac{D_L}{x_L} (c_i - c_o) \qquad (14)$$

where

$$k_L = \frac{D_L}{x_L} \qquad (15)$$

Eqs. (12) and (13) are impractical as the p_i and c_i equilibrium relation requires to be known together with both k_G and k_L. Normally an overall coefficient is employed viz.,

$$N_a = K_G(p_o - p_e) = K_L(c_e - c_o) \qquad)16)$$

where

p_e is partial pressure in equilibrium with solution conc. c_o

and

p_o do. do. c_e

Overall coefficients can only be used where the equilibrium curve is a straight line. If this

equilibrium/

equilibrium relation can be represented by Henry's Law then

$$p_e = H.c_o \qquad \text{(17)}$$

where H = Henry's Law constant

A relationship between the overall and the individual film coefficients can then be established from Eqs. (12), (13), (16), (17) viz.,

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \qquad \text{(18)}$$

&

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \qquad \text{(19)}$$

These formulae are known as the rule for "addition of resistances" in series[20] because it is seen that the reciprocal of the overall coefficient is equal to the sum of the reciprocal of the individual coefficients. It may be looked upon as $1/K_G$ representing the overall resistance to mass transfer by diffusion from gas to liquid phases, $1/k_G$ the gas film resistance and H/k_L the liquid film resistance, all in terms of pressures. Similarly in terms of liquid concentrations $1/K_L$ is the overall resistance $1/k_L$ the liquid film resistance and $1/Hk_G$ the gas film resistance. It will be seen from Eqs. (18) and (19) that if H is very small then the liquid/

liquid film resistance will be negligible compared with the gas film resistance. As H is a measure of the solubility of the gas it follows that for a very soluble gas the gas film controls. Conversely for a slightly soluble gas the controlling film is that in the liquid.

Although it has been in use for over thirty years for the estimation of the overall coefficients used in design, the validity of the two film theory has never quite been established. This is probably due to the experimental difficulty in establishing the individual coefficients for many systems. In some cases the rule for addition of resistances seems to have been proved, in others the actual concept appears to be erroneous.

Now the Whitman theory assumes that surface films are of negligible capacity compared to the amount diffusing through them and all the formulae is deduced on this assumption. However, at the instant a gas and liquid are brought into contact the liquid surface is itself fresh and requires a certain time in order to allow the dissolved gas to penetrate the liquid film. The diagram (Fig. 3) indicates the penetration depth in the form of concentration levels at successive time intervals/

intervals (dotted lines). If this penetration process is not interupted the concentration level is reached at which the Whitman theory becomes valid. Thus if an industrial absorber has contact times shorter than that required for Whitman film conditions to form, then some discrepancies on the basis of this film theory will be observed.

The Higbie theory[4] assumes that liquid running down a packing is in streamline flow in the outer layer and perfectly mixed in the region adjacent to the packing. As the liquid meets some irregularity on the packing surface, or is checked by some other cause, the layer is disrupted and complete remixing takes place for an instant, after which laminar, but completely fresh, layers again exist. These disruptions are assumed to occur at regular intervals and thus each element of liquid element surface is exposed to the gas for the same length of time and absorbs gas at the same rate as a stagnant layer of infinite depth. Application of mathematics to the above absorption mechanism picture is by the so-called "penetration theory".[21,22]

A gas diffuses through a liquid according to Ficks'

or/

or Graham's Law

$$\frac{\partial c}{\partial t} = D_L \cdot \frac{\partial^2 c}{\partial x^2} \qquad \text{(20)}$$

Heat effects, surface effects and expansion are neglected, the diffusion coefficient D_L is assumed constant and the depth infinite

when $c = c_o,\ x > 0,\ t = 0$

$c = c_e,\ x = 0,\ t \geqslant 0$

$c = c_o,\ x = \infty,\ t \geqslant 0$

Under these end conditions the concentration is given by

$$c = c_o + \frac{(c_e - c_o)}{\sqrt{D_L t \pi}} \int_x^{\infty} e^{-x^2/4D_L t} \cdot dx \qquad \text{(21)}$$

whence F the amount of gas absorbed upto time t_e is

$$F = 2(c_e - c_o)\sqrt{\frac{D_L t_e}{\pi}}$$

$$\therefore \quad N_a = 2(c_e - c_o)\sqrt{\frac{D_L}{\pi t_e}} \qquad \text{(22)}$$

and the liquid film coefficient in concentration units is

$$k_L = 2\sqrt{\frac{D_L}{\pi t_e}} \qquad \text{(23)}$$

which varies inversely as the square root of the exposure time./

time. This is consistent with experimental data, in that increases in turbulence, and shortening of exposure time, result in larger apparent film coefficients.

It was this constant exposure period, hardly conceivable in many types of absorption equipment, that led Danckwerts[5] to modify Higbie's conception of the mechanism of absorption by suggesting that the process of production of fresh surface was irregular rather than regular. This appears to offer a more feasible explanation of the process, especially when applied to certain industrial units, yet it will be noted that Danckwerts' rate of surface renewal, reduces to Higbie's exposure time factor when certain fundamental laboratory techniques are considered.[23] The mechanism picture of the Danckwerts theory considers a turbulent liquid mass surface which is continually, but in random fashion, exposing fresh areas of surface to the gas by reason of internal eddies, with the aged surface being swept away below and mixing with the bulk of the liquid. The rate at which mass transfer takes place through these fresh surfaces is assumed to be given by the penetration theory as in the Higbie model.

Considering the Danckwerts idea on a mathematical basis/

basis, assumes the liquid mass to be kept in turbulence by means of stirring at a steady rate, and the liquid area offered to the gas is taken as unity. The average absorption rate over this area, and the mean rate at which surface renewal, S, takes place are assumed constant - the chance of replacement of a surface element by another within a given time is assumed to be independent of its age. Let the area of surface comprising these elements having ages between t and (t + dt) be φ (t)dt. As this is independent of time, at steady state conditions, in a short time interval dt the area entering the age group t....(t + dt) from the age group (t - dt)....t will be φ (t)dt. This also equals the area in age group (t - dt)....t less the portion replaced by fresh surface in a time equal to dt i.e.

$$\varphi(t)dt = \varphi(t - dt)\ dt(1 - S.dt)$$

Therefore

$$\varphi(t) = \varphi(t) - \frac{d\varphi}{dt} . dt - S.\varphi(t).dt$$

$$\& \quad \frac{d}{dt} = - S.\varphi$$

Since also $\int_0^\infty \varphi . dt = 1$

$$\varphi = S.e^{-St} \qquad (24)$$

For areas other than unity, $\varphi(t).dt$ is equal to the fraction of the area which at steady state is in the age group t....(t + dt). φ t is referred to here as the age distribution function. Now as the rate of absorption into the fresh surface is governed by the penetration theory its value here, when considered as operating on all elements having age t and combined area $S.e^{-St}.dt$, is given by

$$(c_e - c_o)\ S.e^{-St} \sqrt{\frac{D_L}{\pi t}}\ .dt$$

Hence the mean rate of absorption per unit is

$$N_a = (c_e - c_o) \sqrt{D_L} \int_o^{\infty} \frac{S.e^{-St}}{\sqrt{\pi t}}\ .dt$$

$$\therefore \quad N_a = (c_e - c_o) \sqrt{D_L S} \qquad \text{(25)}$$

Again from (12)

$$k_L = \sqrt{D_L S} \qquad \text{(26)}$$

It is seen that this mathematical analysis derives the rate of absorption for liquid film resistance only, but if the gas film and a potential surface resistance are considered then the rule for "addition of resistances", as arrived at from the Whitman theory, can be shown to apply/

apply. The actual expression for the overall transfer is

$$N_a = \frac{c_e - c_o}{\frac{1}{\sqrt{D_L S}} + \frac{H}{k_G} + \frac{1}{k_S}} \qquad (27)$$

The denominator can be identified with equations (18) and (19). In comparing the two theories i.e. the two film and the penetration, it is noticed that only the liquid film coefficient in physical absorption has been theoretically investigated - the gas film coefficient being treated more from a kinetic or empirical point of view[24]. Thus an illustration is given on the basis of a hypothetical liquid film controlled system (Fig. 4). The case is exaggerated but it is evident that the Whitman theory is independent of time - the coefficient being equal to the diffusivity divided by the thickness of the film whilst the Higbie-Danckwerts theory gives a coefficient varying as $\sqrt{\frac{D_L}{\pi t_e}}$ if no surface renewal takes place. A third curve shows what Higbie calls a first order process at the surface (a surface resistance) and it is this curve which shows best agreement with the experimental data of both Higbie[4] and Danckwerts[23] for the carbon-dioxide water/

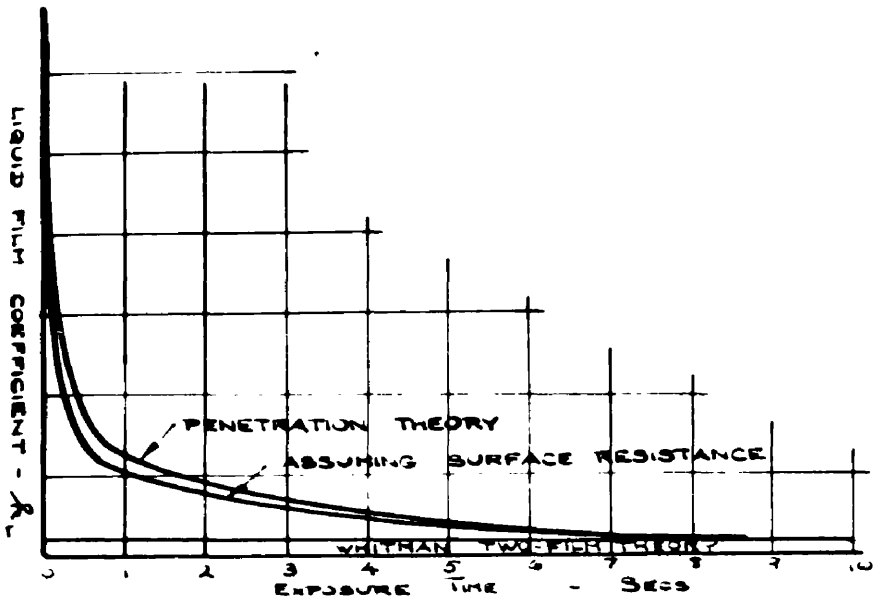

LIQUID FILM COEFFICIENT - k_L
PENETRATION THEORY
ASSUMING SURFACE RESISTANCE
WHITMAN TWO-FILM THEORY
0 1 2 3 4 5 6 7 8 9 10
EXPOSURE TIME - SECS

FIG. 4

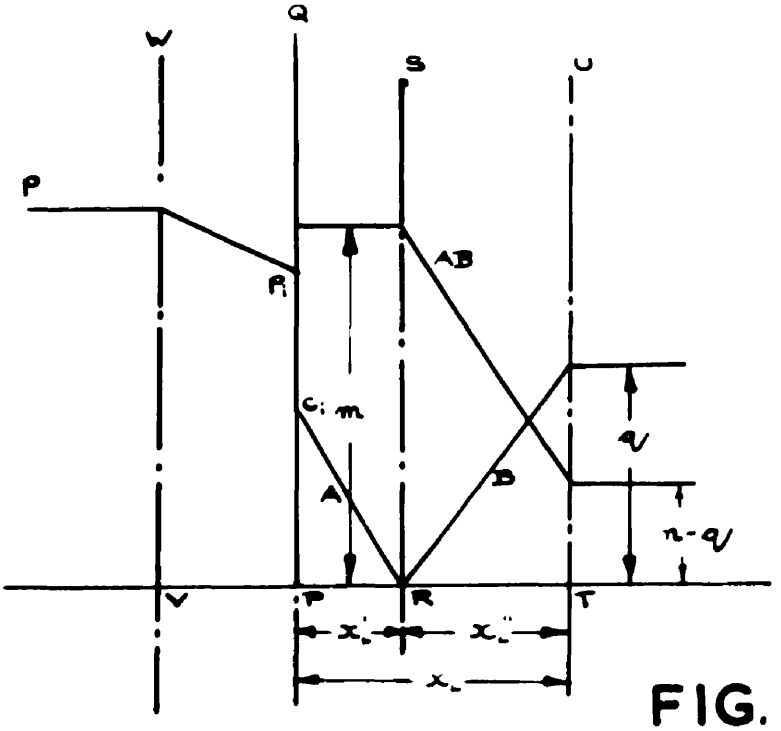

W
Q
S
U
P
P_i
AB
C_i m
A
B
q
n-q
V
P
R
T
x_L'
x_L''
x_L

FIG. 5

water system.

Consider now gas absorption with chemical reaction, a process which has advantages over physical absorption owing to the large absorption capacity of the solution, and a reduced resistance of absorbed material in the solution. The first application of the two-film theory to chemical absorption was made by Hatta[25,26] in 1929. Under conditions of steady state diffusion, there is the effect of removal of diffusing molecules by chemical reaction in the liquid film in addition to the diffusional resistance in the gas and liquid films. It is also essential to allow for the diffusion rate at which the absorption medium molecules arrive at the reaction zone.

Consider a mathematical analysis of a chemical reaction absorption process in the light of the "two-film" theory. For example, assume that a solute gas A is absorbed from a gas mixture by a solution of a substance B which combines with A according to the equation

$$A + B \longrightarrow AB$$

(The reaction is considered as rapid, irreversible and of the second order) and Fig. 5 shows a sketch of the/

the concentration gradients after the equilibrium reactive position is reached. PQ represents the place of the interface between the gas and liquid phases. VW and UT form the demarcation lines of the gas and liquid films respectively. SR indicates the reaction equilibrium line, to which A & B diffuse and from which the product AB diffuses towards the bulk of the liquid. The driving force $(p - p_i)$ causes A to diffuse through the gas film whilst the driving force c_i in the liquid phase induces diffusion toward the reaction zone. B diffuses from the bulk of the liquid to the reaction zone under the driving force of q, and the reaction products diffuse back into the bulk of the liquid under the potential $m -(n - q)$. q denotes the normality of B in the solution and n the normality of free plus combined B, thus the normality with respect to AB is $n - q$. As the reaction products tend to diffuse in both directions AB is assumed non volatile, and RS is considered as containing a uniform concentration of AB because the process is rapid. Thus for the gas film

$$N_A = k_G (p_o - p_i) \qquad (28)$$

and/

and assuming the solvent concentration to be large compared with the concentration of A, B and AB the above equation may be written

$$N_A = \frac{D_A}{x_L'} (c_i - 0) \qquad (29)$$

for the first section of the liquid film. For other remaining section SV,

$$-N_B = \frac{D_B}{x_L''} (q - 0) = +N_A \qquad (30)$$

$$\& \qquad N_{AB} = \frac{D_{AB}}{x_L''} (m - n + q) = N_A \qquad (31)$$

Now as A is dissolved physically in the QS section and equilibrium is assumed to exist at the interface QP, then Henry's Law is held to apply approximately,

$$p_i = Hc_i \qquad (32)$$

and by combining equations (30) and (31)

$$m - (n - q) = \frac{D_B}{D_{AB}} \cdot q \qquad (33)$$

Now Eqs. (28), (30) and (32) may be combined to eliminate p_i, c_i, m, n, x_L' and x_L'' giving

$$N_A = \frac{(p/H) + (D_B/D_A)q}{(x_L/D_A) + (1/Hk_G)} \qquad (34)$$

The/

The form of the equation is noted to be similar to the physical absorption process with the numerator expressing the driving force. Eq. (34) in terms of the more useful liquid film conditions is

$$N_A = \frac{c_{Ai} + (D_B/D_A)q}{x_L/D_A} \qquad (35)$$

And if a liquid film coefficient is defined on the basis of the driving force ($c_{Ai} - 0$) we have

$$k_L = \frac{D_A}{x_L}\left(1 + \frac{D_B}{D_A} \cdot \frac{q}{C_{Ai}}\right) \qquad (36)$$

Absence of chemical reaction reduces (36) to the quotient $\frac{D_A}{x_L}$ as is the derived formulae for physical absorption and the bracket factor shows the affect of bulk liquid coefficient q on the apparent coefficient.

The derivation of (34) is the same as that of Hatta[25] who considered the analysis from the absorption of carbon dioxide from air into aqueous KOH solution. He found the theory most readily applied to his own experimental technique, although Van Krevelen and Hoftizer[27] report good agreement also. The application of the experimental data obtained to other types of absorption equipment has not proved so successful although/

although this has been the subject of many investigations.

Subsequent theoretical development has followed the Higbie[4] concept of unsteady state molecular diffusion of the gas into the whole mass of the liquid. If the same second order, rapid irreversible reaction is considered in the light of the penetration theory and it is assumed[28] that the reaction rate is extremely high compared with the rate of diffusion of the reactants then the following average rate of absorption is derived

$$(N_A)_{ave} = \frac{2.c_{Ai}}{\mathrm{erf}(\sqrt{}/D_A)} \cdot \sqrt{\frac{D_A}{\pi.t_e}} \qquad \text{(37)}$$

and if a liquid film coefficient is considered then

$$k_L = \frac{2}{\mathrm{erf}(\sqrt{}/D_A)^{\frac{1}{2}}} \cdot \sqrt{\frac{D_A}{\pi.t_e}} \qquad \text{(38)}$$

or if D_A is assumed equal to D_B then

$$k_L = \left(1 + \frac{q}{C_{Ai}}\right) 2.\sqrt{\frac{D_A}{\pi.t_e}} \qquad \text{(39)}$$

The unsteady state analysis of the irreversible second order reactions following the Higbie-Danckwerts concept has the advantage over Hatta's in allowing for the flow of the liquid film as absorption proceeds.

It is convenient at this stage of the synopsis

to/

to introduce the first conception of absorption kinetics as introduced by Kishinevski and Pamilov[6,7]. Their expressions may be applied to both absorption with chemical reaction and ordinary physical absorption. In the latter case, an equation very similar to Whitman's earlier expression can be deduced. High turbulence is defined as turbulence continually breaking the surface at the interface[29] and not dying down as is supposed in the two film theory. In such systems, in which high turbulence is present with reacting phases, they suggest the transfer of a substance towards the interface as a mass flow mechanism and they introduce the concept not only of the period required for surface renewal, as in the Higbie-Danckwerts theory, but also of the degree of neutralisation of the surface layer, in order to express the mass-transfer rate quantitatively. Their concept of high and low turbulence is defined by the velocity of the chemical reaction as well as by the hydrodynamics of a system. Complete neutralisation (i.e. low turbulence) may occur for similar hydrodynamic conditions as would allow, in a slow reaction, incomplete neutralisation (high turbulence). Although these workers are still in the process of developing their theory/

theory for all absorptive processes, the development of an agreed equation applicable to first and second order reaction, as well as to physical absorption, will be given below.

Consider a process involving a first order reaction in which the solubility of the gas in the surface layer is practically independent of its degree of neutralisation and consequently remains unchanged during the whole renewal period of the surface layer. The renewal period of the surface layer is t_e and the degree of neutralisation of this layer by, η . The absorption rate is determined (in the liquid phase) by the equation

$$N_a = V_n \ (m_s \cdot \eta \cdot c) + c_i \qquad \text{(40)}$$

m_s = coefficient dependent upon the stoichiometric equation of the chemical reaction

where

V_n = hydrodynamic constant of the liquid phase or linear velocity of mass flow in the direction normal to the interface ϕk_L

$m_s \cdot \eta \cdot c$ = the concentration of the molecules of the absorbed gas chemically bound in the surface layer

c_i = the concentration of physically disolved free molecules in the surface layer.

Now the concentration of the free molecules in the surface/

surface layer, c_i is related to the partial pressure of the gas at the interface p_i by Henry's Law, i.e.

$$p_i = H.c_i \qquad \text{(41)}$$

Since it has been assumed that the reaction in the surface layer follows the first order, the degree of neutralisation of the surface layer can easily be expressed by the concentration of the chemically active component of the solution at the initial moment of reaction. Thus for a first order reaction

$$\frac{c}{c - x_1} = K'.t \qquad \text{(42)}$$

where c is the initial concentration of the reacting substance in this case the chemically active component in the solution; $c - x_1$ is the concentration of substance at time t; and K' is the first order reaction constant proportional to the almost unchanging concentration of free molecules of the gas in the surface layer. Since interest lies in the concentration of the chemically active components of the solution in the surface layer towards the end of its renewal period, t must be replaced in formulae (42) by t_e (the

fractional/

fractional time of renewal).

On the other hand

$$c - x = (1 - \eta)\, c \qquad \text{(43)}$$

Substituting (43) in (42) and solving with respect to η

$$\eta = 1 - e^{-K' \cdot t_e} \qquad \text{(44)}$$

by using the expansion of series method.

In agreement with what has been said above

$$K' = K_c c_i \qquad \text{(45)}$$

where K_c equals second order reaction rate constant.

After substituting the relationships obtained in Eq. (40) the formulae for absorption rate assumes the following form;

$$N_a = V_n \left[m(1 - e^{-K_c \cdot c_i t_e})\, c + c_i \right] \qquad \text{(46)}$$

Now the equation for mass transfer in the gaseous phase is

$$N_a = \beta\, (p - p_i) \qquad \text{(47)}$$

where β = "hydrodynamic constant of the gaseous phase"

and p = partial pressure of the absorbed gas

Thus/

Thus combining Eqs. (41), (46) and (47) with elimination of surface conditions, an equation is obtained for the absorption rate defined by its basic parameters:

$$N_a = \frac{m_c \left[1 - e^{-(p - N_a/\beta)\,(K_c/H)t_e}\right] + p/H}{\frac{1}{V_n} + \frac{1}{\beta.H}} \quad (48)$$

The equation is given in its implicit form. It can, however, be readily solved graphically. Its range of application covers any value of t_e over varying between zero and unity. Now in analysing Eq. (48), and considering the condition of high turbulence in which t_e is very small, it will be seen that if $e^{-(p - N_a/\beta)\,(K_c/H).t_e}$ is expanded and the first order term only is included then

$$e^{-(p - N_a/\beta)\,(K_c/H).t_e} = 1 - (p - N_a/\beta)\,(K_c/H).t_e$$

and substituting in Eq. (48) and solving w.r.t. N_a then

$$N_a = \beta.p.\left[\frac{K.c + V_n}{K.c + V_n + \beta/H}\right] \quad (49)$$

where $K = K_c.m_s.t_e.V_n$

This equation describes the limiting case of absorption at high turbulence with negligible neutralisation/

neutralisation of the surface layer. The other extreme considers decrease in turbulence of the liquid phase and a corresponding increase of t_e with

$$e^{-(p - N_a/\beta)\,(K_c/H).t_e} \longrightarrow 0$$

Thus the degree of neutralisation of the surface layer tends to unity and Eq. (48) becomes

$$N_a = \frac{m_s c + p/H}{1/V_n + 1/\beta . H} \qquad \text{(50)}$$

Eqs. (49) and (50) are considered as the limiting cases, under conditions of high turbulence, of absorption accompanied by chemical reaction. It will be noted that Eq. (50) is formally identical with that deduced by Hatta[25] on the basis of the two film concept.

For purely physical absorption processes, the following three equations are presented

$$p_i = H.c_i \qquad \text{(a)}$$

$$N_a = \beta\,(p - p_i) \qquad \text{(b)}$$

$$N_a = V_n(c_i - c) \qquad \text{(c)}$$

to give

$$N_a = \frac{p/H + c}{1/\beta . H + 1/V_n} \qquad \text{(51)}$$

on elimination of p_i and c_i

This/

This approach gives a similar result to the two film theory and does not consider "exposure time" as in the Higbie-Danckwerts approach. (ϕ Eqn. Below)

$$\left(N_a = \frac{c_e - c_o}{1/k_L + 1/Hkg} \right)$$

However, in more recent papers Kishinevski[8,9,10] develops his theory further by introducing an "effective" diffusion coefficient and defines it as a summation of molecular diffusion D_L and eddy diffusion E_L. His theoretical picture considers diffusion of mass from the interface into the depth of the turbulent stream, assuming that the second border exists at infinity, because the depth of the turbulent stream which is absorbing gas is many times greater than the hypothetical diffusion layer. Conditions for this problem can be written as a differential equation.

$$\frac{\partial c}{\partial t} = \left[D_L + E_L(x) \right] \frac{\partial^2 c}{\partial x^2} + \frac{\partial c}{\partial x} \cdot \frac{\partial (E_L)}{\partial x} \qquad \text{——— (52)}$$

with the following end conditions

$$\left.\begin{aligned} c &= c_e \text{ if } x = 0 \text{ and } t \geqslant 0 \\ c &= c_o \text{ if } x = \infty \text{ and } t \geqslant 0 \\ c &= c_o \text{ if } x > 0 \text{ and } t = 0 \end{aligned}\right\} \qquad \text{——— (53)}$$

$E_L(x)$/

$E_L(x)$ denotes the dependence of E_L on the distance from the interface and it is the difficulty in establishing the relationship between E_L and x, either theoretically or experimentally, as well as the considerable difficulty involved in solving Eq. (52) that makes Kishinevski assume $D_T = D_L + E_L(x) = \text{constant}$. This assumption is considered to have adequate foundation because in industrial equipment contact times of gas and fresh liquid surfaces are very short and during this interval of time only a small depth of penetration can be achieved. Then changes in E_L within limit of a small value of x are considered as negligible. Thus

$$\frac{\partial c}{\partial t} = D_T \cdot \frac{\partial^2 c}{\partial x^2} \qquad (54)$$

This is a modification of Higbie's penetration theory, which is not mentioned by the author, in that D_T - the combined diffusion coefficient is used rather than the molecular diffusivity. Solution of this equation gives

$$k_L = \sqrt{\frac{4D_T}{\pi \cdot t_e}} \qquad (55)$$

Thus it appears as if Kishinevski's theoretical approach varies/

varies from Higbie's in that an "effective" diffusivity is used in preference to a molecular one (not without some just cause from a physical interpretation of the mechanism of the absorption process).

Thus the four main concepts of the mechanism of gas absorption have been stated in detail. A summary of the main differences can be given in the form of Eqs. (15), (23), (26), (55) which denote the liquid film resistances i.e.

Whitman $\quad k_L = \frac{D_L}{\alpha_L}$

Higbie $\quad k_L = 2\sqrt{\frac{D_L}{\pi . t_e}}$

Danckwerts $\quad k_L = \sqrt{D_L S}$

Kishinevski $\quad k_L = 2\sqrt{\frac{D_T}{\pi . t_e}}$

In order to establish any one of those theories as correct it will be necessary to see how well experimental data fits into the form suggested by other theories. Now it was noted above that the Whitman theory suggests gas absorption coefficients as independent of time. Many experimentalists have attacked this conception and it is fairly well established that the absorption rate/

rate in mols absorbed/(unit area)(unit time) increases as the contact time of the gas and liquid decreases. However, a recent paper by Goodgame and Sherwood[30] suggests that the method of film resistance addition can still be used for design purposes. In these experiments the evaporation of water into air gives an overall coefficient K_G which is determined solely by k_G the gas film coefficient. In the same experimental set up, carbon dioxide is absorbed by water, and this system shows almost complete liquid film control, i.e. $K_L = k_L$. Fixed basis values, then, are established for both gas and liquid films. An equation is then set up for calculation of these coefficients when other solvents and gaseous solutes are used, thus

$$\frac{1}{K_L} = \frac{1}{H.(k_G)_{H_2O}.\left[\frac{D_V}{D_{V(H_2O)}}\right]^{\frac{1}{2}}} + \frac{1}{(k_L)_{CO_2}\left[\frac{D_L}{(D_L)_{CO_2}}\right]^{\frac{1}{2}}} \quad \text{---} \quad (56)$$

The authors give results for the absorption of ammonia and acetone into water, and for ammonia into dilute sulphuric acid, both calculated by their equations and observed. These figures are set out below/

below

	Experimental		Calculated	
	K_G	K_L	K_G	K_L
H_2O Vapour	.203	-	-	-
Absorption of CO_2	-	3.62	-	-
do. NH_3	-	1.69	-	1.76
do. Acetone	-	1.93	-	1.89
do. NH_3 by H_2SO_4	.182	-	0.192	-

Thus it appears that the film theory can still be used with some degree of confidence in design practice. Indeed it is one of the draw backs of the Higbie-Danckwerts theory that a design procedure has still to be established from this concept. However, there appears little doubt that the suggested penetration mechanism holds for certain laboratory techniques - the wetted wall system in particular. Lynn, Straatemeier and Kramers[31] studied absorption of SO_2 into water as a case of physical absorption and applied the penetration theory to the system. Their apparatus took the form of a long wetted wall column, a short wetted wall column (FIG 6a) and single wetted spheres. Agreement with the theory is excellent for the long column (12 - 22 cms.) but not so convincing for the short column (1 - 5 cms.) and/

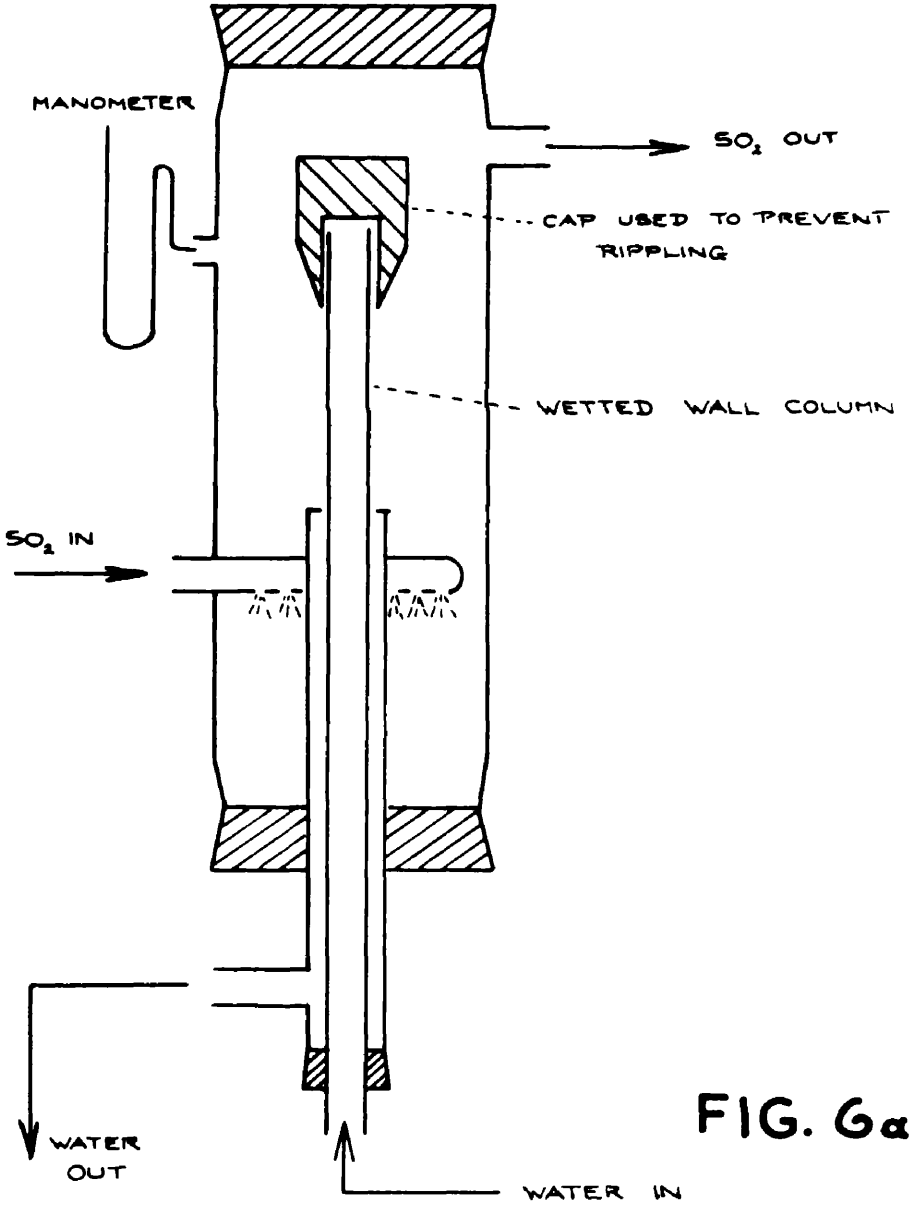

MANOMETER
SO_2 OUT
CAP USED TO PREVENT RIPPLING
WETTED WALL COLUMN
SO_2 IN
WATER OUT
WATER IN

FIG. 6α

and although all the water solutions contained "teepol", a surface active agent which tends to reduce rippling effects common to such absorbers, the end effects are quite pronounced, particularly at the shorter lengths. Vivian and Peaceman[32], however, using a short column (FIG 6b) eliminated both ripples and end effects by special constructional details (see Fig. 6b). The work was carried out with desorption of CO_2 from water and chlorine from diluted HCl (.16 to .18N) and the estimation of the end effects due to temperature, gas rate, and apparatus dimensions was very thoroughly carried out. Their results again proved the validity of the Higbie mechanism to within the limits that can be expected from small scale experiments - the problem in all experimental techniques of this kind is to produce a fresh liquid surface without turbulence or velocity changes of some description at the point of formation. The authors also propose an empirical equation for estimation of liquid film coefficients of systems where the viscosity and density are different from those of water but suggest that it should be used with caution as it has not been proved experimentally.

Many/

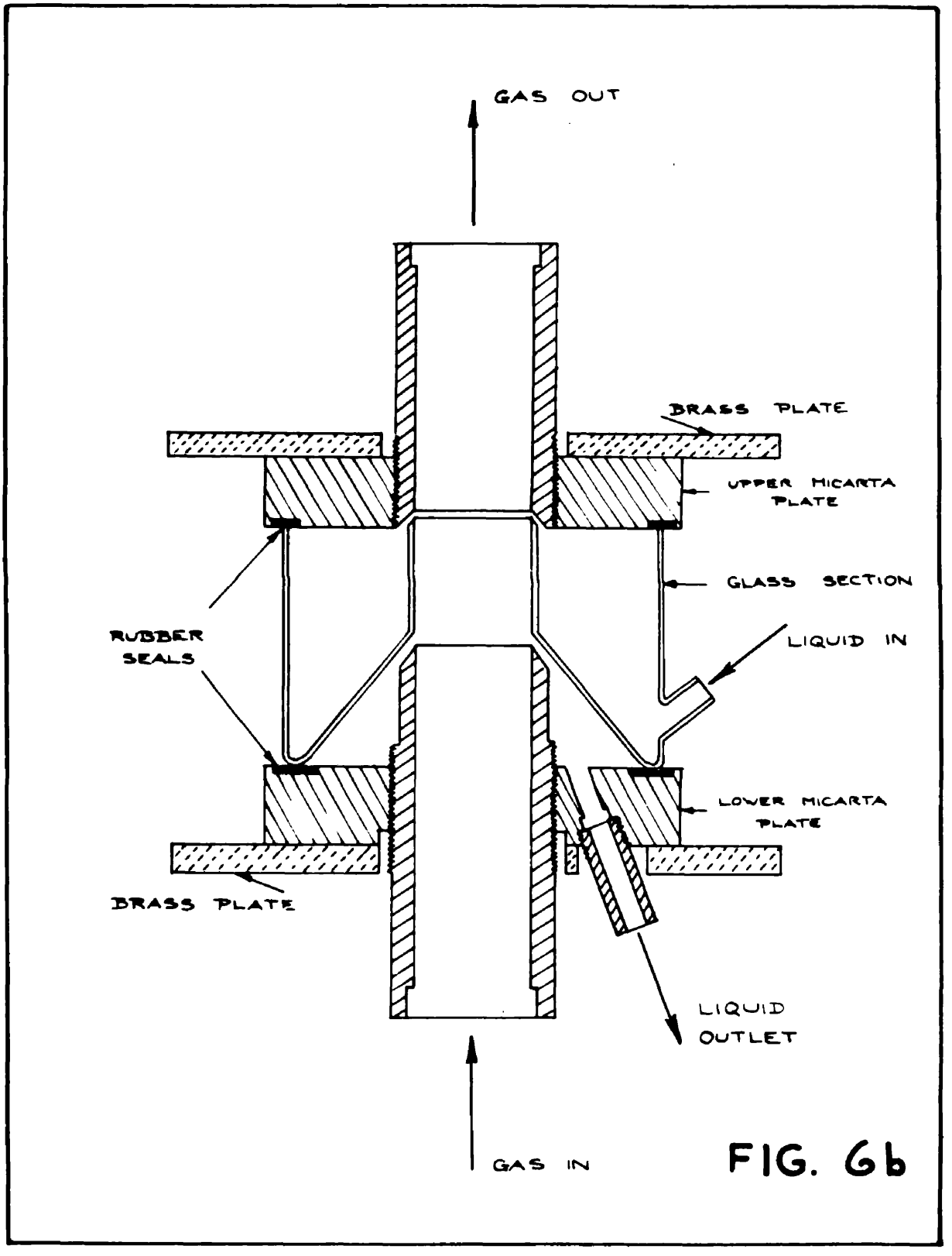

GAS OUT
BRASS PLATE
UPPER MICARTA PLATE
GLASS SECTION
LIQUID IN
RUBBER SEALS
LOWER MICARTA PLATE
BRASS PLATE
LIQUID OUTLET
GAS IN

FIG. 6b

Many other workers[33,34,35] have utilised the wetted wall column in attempts to throw light on the mechanism of gasabsorption, as it represents a technique where the interfacial area is almost fixed and gas phase conditions are reproducible. Other types of equipment have been utilised. Thus, Higbie's own apparatus[4] for quantitative verification of his theory made use of a long capsule shaped bubble forced downwards through a vertical glass tube full of liquid. It was argued that a layer of liquid coated the inside of the tube around the bubble and was held stationary until the bubble has passed. This was claimed to give times of exposure of the order of 0.01 seconds. Unfortunately measurements were confined to the system carbon dioxide-water and possible effects of chemical change ignored.

Higbie's results were slightly lower than those predicted by theory, which argued a definite resistance at the interface. Some evidence for surface resistance had been noted both before[21,22,36,37] and after Higbie's work - Danckwerts[23] in particular assumed a surface transfer coefficient to correlate his own results with those predicted by his theory. In this series of determinations an experimental absorber was used in which/

which transient times of exposure could be achieved by means of a liquid film on a rotating drum. Apart from the carbon dioxide-water system, he investigated other absorption processes involving chemical reaction, viz., CO_2 into solution of Mg_2SO_4, Na_2SO_4, NaOH and buffer solutions. Agreement with the theory in these cases is limited because of the complexity of actual kinetics of the process, but by comparing these results with results obtained in a packed column he concludes that neither the penetration theory nor the two-film theory can be applied with great certainty to design problems.

Another experimental unit is the disc column (FIG 6c) which attempts to simulate the conditions found in a packed column. This idea was evolved by Stephens and Morris[38] and a further development[39] led to a method of evaluating liquid film coefficients for physical absorption processes. Work by Roper[40,41] suggests that neither the film theory nor the penetration theory are substantiated by his disc column results. This could be due to the difficulty in obtaining an even film over the discs with the resultant misapplication of/

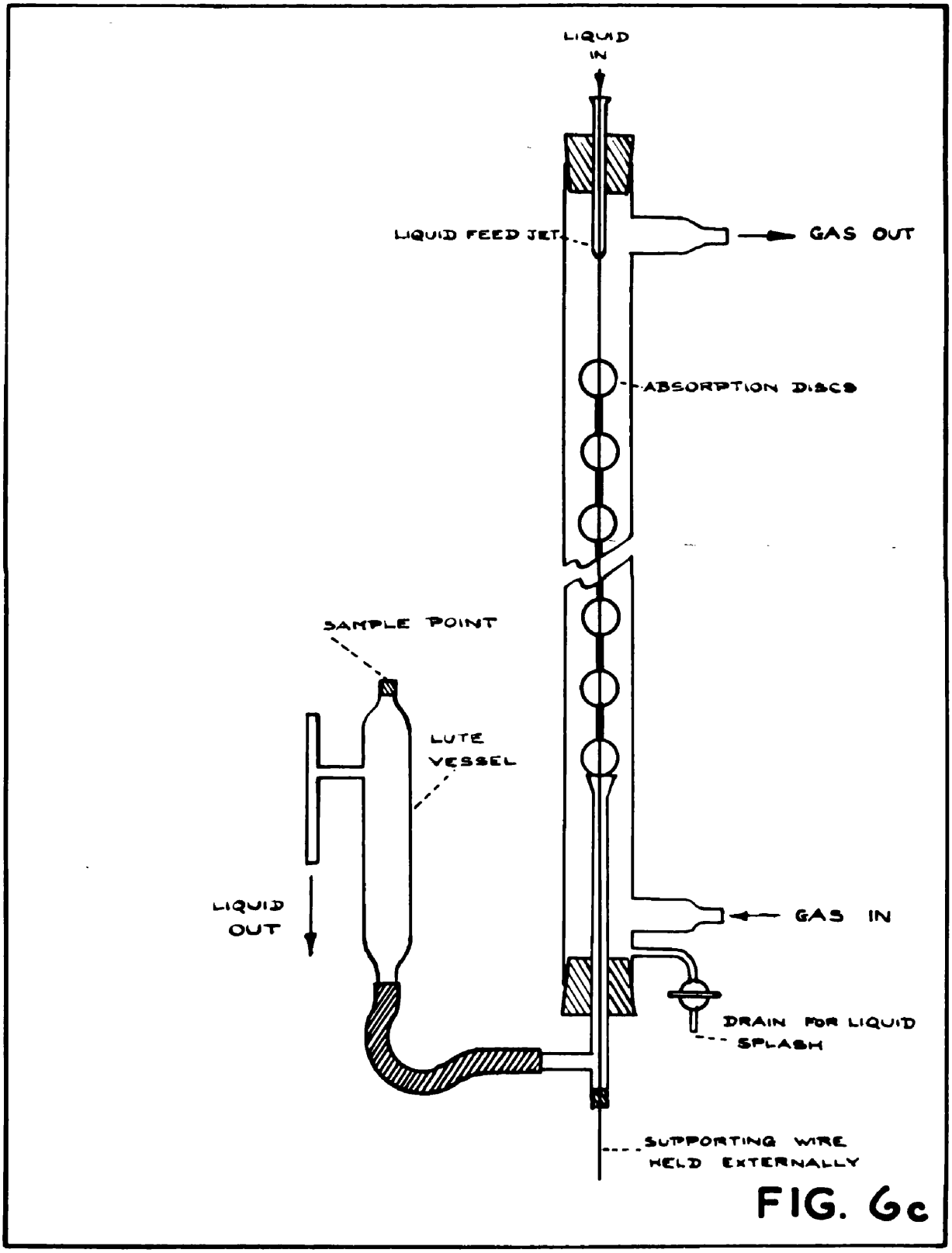

LIQUID IN
LIQUID FEED JET
GAS OUT
ABSORPTION DISCS
SAMPLE POINT
LUTE VESSEL
LIQUID OUT
GAS IN
DRAIN FOR LIQUID SPLASH
SUPPORTING WIRE HELD EXTERNALLY

FIG. 6c

of the theories to an indefinite area of liquid surface. This difficulty is apparently overcome in the work of Lynn et al.[42] who used spheres in place of discs. A laminar film was ensured by addition of .05% wt. of "teepol". Results by these workers show evidence again of the applicability of the penetration theory even allowing for the stretching effect at the maximum sphere section. There is also evidence that no remixing takes place at the discontinuity between any two spheres and the deviation of their results at greater sphere numbers is attributed to rippling effects on the lower spheres. Danckwerts[43] comments on the effect of discontinuities on flow patterns and suggests that the reason for discrepancies arising from application of the penetration theory to packed columns or any other type of industrial absorber in which a similar flow pattern exists may lie in the fact that the actual surface layer is never disturbed. The only effect of passing over a discontinuity is to change the deeper concentration levels to a lower uniform value giving an increase in absorption rate - but not so big an increase as to suggest complete remixing of the surface layer[44,23].

Other/

Other methods of experimental approach, tried by workers in order to establish the theoretical mechanism of absorption, involve a study of liquid jets, droplets or bubbles.

The jet technique is a comparatively new idea but results indicate that the penetration theory can be applied with a fair degree of certainty. Matsuyama[45] correlated his data quite successfully by means of the theory and Cullen and Davidson[46] worked out a hydrodynamic correlation based on the mass and momentum analogy which resulted in the mass transfer coefficient being inversely proportional to the square root of the exposure time. It is strange to note that Cullen and Davidson do not mention the similarity of their formulae to the Higbie conception. Their work was carried out on the carbon dioxide-water system in a special jet nozzle arrangement which ensured rod like flow and thus prevented the formation of ripples which appear under streamline flow conditions just below the jet tip. Addition of surface active agents is another method of suppressing the rippling effect[47,48] which results in decrease of the absorption to a slight degree. Rumford et al.[49] also noted that a shorter

exposure/

exposure time gave increased transfer coefficients for the CO_2-NH_4OH system but their results were relatively unaffected by addition of surface active agents and suggest a rather higher power function of the exposure time - 0.8 as compared to the normal 0.5.

Evidence from absorption work with droplets is rather confusing. In early work, absorption of carbon dioxide by drops of water was carried out by Whitman et al.[50] in a constant length column, They varied time of formation and estimated the gas absorbed during free fall by extrapolation to zero formation time. Assuming this to be constant they calculated absorption rates during formation by subtracting this constant value from the total amount absorbed and found relatively small absorption during formation. However, Dixon and Russell[51] suggest that this method is not sound and their results show that the rate of absorption during free fall increases when rate of formation of the droplets is increased. The results below show the anomaly more clearly

	Time (Secs.)	Whitman et al. (K_L)	Dixon & Russell (K_L)
During formation	.5	4.4	113
	5	4.1	20.5
During fall	.5	269	106
	5	338	32

Dixon/

Dixon and Russell correlate their results for drops during time of formation in the form $K_L = \frac{k_1(\Delta + k_2)}{t_e^{0.8}}$ - being the turbulence factor of the droplet, which varies with the type of jet and rate of formation of droplets. These results (and Hatta's[52] high diffusivity figures during free fall) are suggested as being due to turbulence, either in the interior of the drop or on the outside layer caused by gas flow past the fallen drop. Other workers[53,54] show that for absorption of carbon dioxide into liquid droplets, the amount absorbed varies as the square root of the exposure time during fall from rest but they do not suggest any formation time effects. Recent work by Groothuis and Kramers[55] on rates of absorption during droplet formation (1 - 40 seconds) utilise a simplified form of the penetration theory in correlation of the results. Their apparatus is cleverly arranged for production of a uniform rate of drop formation by means of a synchronous motor driven screw plunger.

Bubble absorption rates are very difficult to asses due to the complex mechanism of liquid flow round the bubble causing circulation within the bubble itself./

itself. Most of the recent work has been done by Garner et al.[56,57] who state that Higbie's equation appears to hold approximately although unfounded assumptions have been used in its development. Their work covers the mechanisms of flow patterns and mass transfer in bubbles very thoroughly. By using a series of gases, hydrogen, oxygen, ethane, ethylene and carbon dioxide they confirm the validity of the diffusivity power in the penetration theory as being about 0.5 (actual values .41 - .55) - a power factor also established for wetted wall columns[58] and generally agreed to Sherwood and Holloway[59].

These results are in contradiction to the Kishinevski theory that the molecular diffusivity plays little or no part in the mechanism, while work by Lewis[60] suggests that mass transfer across a liquid-liquid interface under turbulent conditions takes place by eddy and not by molecular diffusion.

A recent German paper has pointed out the dominant effect of surface tension in many liquid-liquid systems, and a film prepared by the same workers demonstrated the eruptive effect of surface tension changes in an amazing manner.

This concludes a resumée of the application of laboratory/

laboratory, and in some cases large scale, techniques to establish the actual mechanism of gas absorption into liquid surfaces. It appears that the validity of Whitman two-film theory is doubtful in view of the evidence of the effect of exposure time on absorption rate. The two film theory can, however, be held to cover this effect by supporting additional turbulence at the point of surface formation and hence thinner films for molecular diffusion. The body of evidence appears to be in favour of the penetration theory. The authors work on absorption will be examined in due course for further light on this point.

NOMENCLATURE for INTRODUCTION

a_1 = Ratio of fluid velocities at boundary of laminar film and in main fluid stream.

a_2 = Constant in Eq. (10).

c = Concentration, lb.mols./ft^3.

c_e = Concentration of solute in liquid in equilibrium with p_o, lb.mols./ft^3.

c_i = Concentration at phase boundary, lb.mols./ft^3.

c_o = Initial concentration of solution, lb.mols./ft^3.

C_{Ai} = Concentration of solute A at the interface, lb.mols./ft^3.

C_p = Specific heat at constant pressure, B.t.u./(lb.)(^{o}F).

D_A = Liquid diffusivity for component A, ft^2/hour.

D_B = Liquid diffusivity for component B, ft^2/hour.

D_{AB} = Liquid diffusivity for reaction product AB, ft^2/hour.

D_L = Molecular diffusivity in liquid, ft^2/hour.

D_T = $D_L + E_L$

D_V = Molecular diffusivity in gas, ft^2/hour.

erf = Mathematical "error function" = $\frac{2}{\sqrt{\pi}} \int_o^{\gamma} e^{-z^2}\, dy$

E = Eddy diffusivity, ft^2/hour

E_L = Eddy diffusivity in liquid, ft^2/hour.

f = Friction factor, dimensionless.

F = Gas absorbed in time t_e, lb.mols./ft^2.

G_m = Molal mass velocity of stream, lb.mols./(hour)/(ft^2).

h = Individual or film coefficient of heat transfer, B.t.u./(hour)/ft.^{2}/^{o}F.

H = Henry's Law Constant = p_e/c_o, lb.mols./(ft.^{3})/atm.

j_D = Mass transfer function = $\frac{1}{2}f$

j_H = Heat transfer function = $\frac{1}{2}f$

k = Thermal conductivity, B.t.u./(hour)/(ft.^{3})/(^{o}F/ft.)

k_1 = Constant in formula p.

k_2 = Constant in formula p.

k_c/

k_c = $k_G R.T.$ = Mass transfer coefficient, lb.mols./(hour)/(ft^2)/(lb.mols./ft^3)

k_G = Individual or gas film coefficient, lb.mols./(hr.)/(ft^2)/(atm.

k_L = Individual or liquid film coefficient, lb.mols./(hour)/(ft^2)/(lb.mols./ft^3)

k_s = Mass transfer coefficient for surface resistance, lb.mols./(hour)/(ft^2)/(lb.mols./ft^3)

K' = First order reaction rate constant.

K_C = Second order reaction rate constant.

K_G = Overall mass transfer coefficient, lb.mols./(hr)/ft^2)/(atm.)

K_L = Overall mass transfer coefficient, lb.mols./(hour)/(ft^2)/(lb.mols./ft^3).

m = Concentration of reaction zone AB, lb.mols./ft^3.

m_s = Coefficient dependent upon the stoichiometric equation of the chemical reaction.

M_m = Average molecular weight of fluid stream.

n = Normality of free + combined component B in solution, lb.mols./ft^3.

N_a = Rate of mass transfer, lb.mols./(hour)/(ft^2).

N_A = Diffusion rate of A, lb.mols./(hour)/(ft^2).

N_B = Diffusion rate of B, lb.mols./(Hour)/(ft^2).

p = Partial pressure of gas in bulk, atm.

p_B = Partial pressure of non-diffusing gas B, atm.

p_{BM} = log. mean of p_B at phase boundary & p_B in bulk.

p_e = Partial pressure of solute gas in equilibrium with c_o, atm.

p_i = Partial pressure of solute gas at interface, atm.

p_o = Partial pressure of solute gas in bulk, atm.

P_T = Total pressure, atm.

q = Normality of B in solution, lb.mols./ft^3.

R = Gas constant, (ft^3)(atm.)/(lb.mol.).(^oR) = 0.728

R_e = Ratio of mean to maximum concentration difference.

R_U = Ratio of average to maximum velocity = U_{av}/U_{mean}

S/

S = Fractional rate of renewal of liquid surface, /(hour).

t = Time after beginning of exposure, hour.

t_e = Time of exposure of surface, hour.

T = Absolute temperature, ^{o}R.

U_{av} = Mean velocity in conduit, ft./hour.

V_n = "Hydrodynamic constant of liquid".

x = Distance in direction of diffusion, ft.

x_L = Thickness of stagnant film, ft.

x_L' = Effective thickness of liquid film from the interface to the reaction zone, ft.

x_L'' = Effective thickness of liquid film from the reaction zone to the bulk of the liquid, ft.

x_l = Decrease in concentration of substance in liquid after time t.

α = $E.\rho./\epsilon$

β = "Hydrodynamic constant of gas".

Δ = Turbulence factor.

ϵ = Eddy viscosity, lb./(hour)(ft.)

φ = Surface renewal function.

φ_b = Denominator of Eq. (8).

ρ = Density, lb./ft^3.

μ = Viscosity, lb./(hour)(ft.)

ψ = $\alpha.\mu/\rho.D_V$ = $E\mu/D_V\epsilon$

η = Degree of neutralisation of liquid layer.

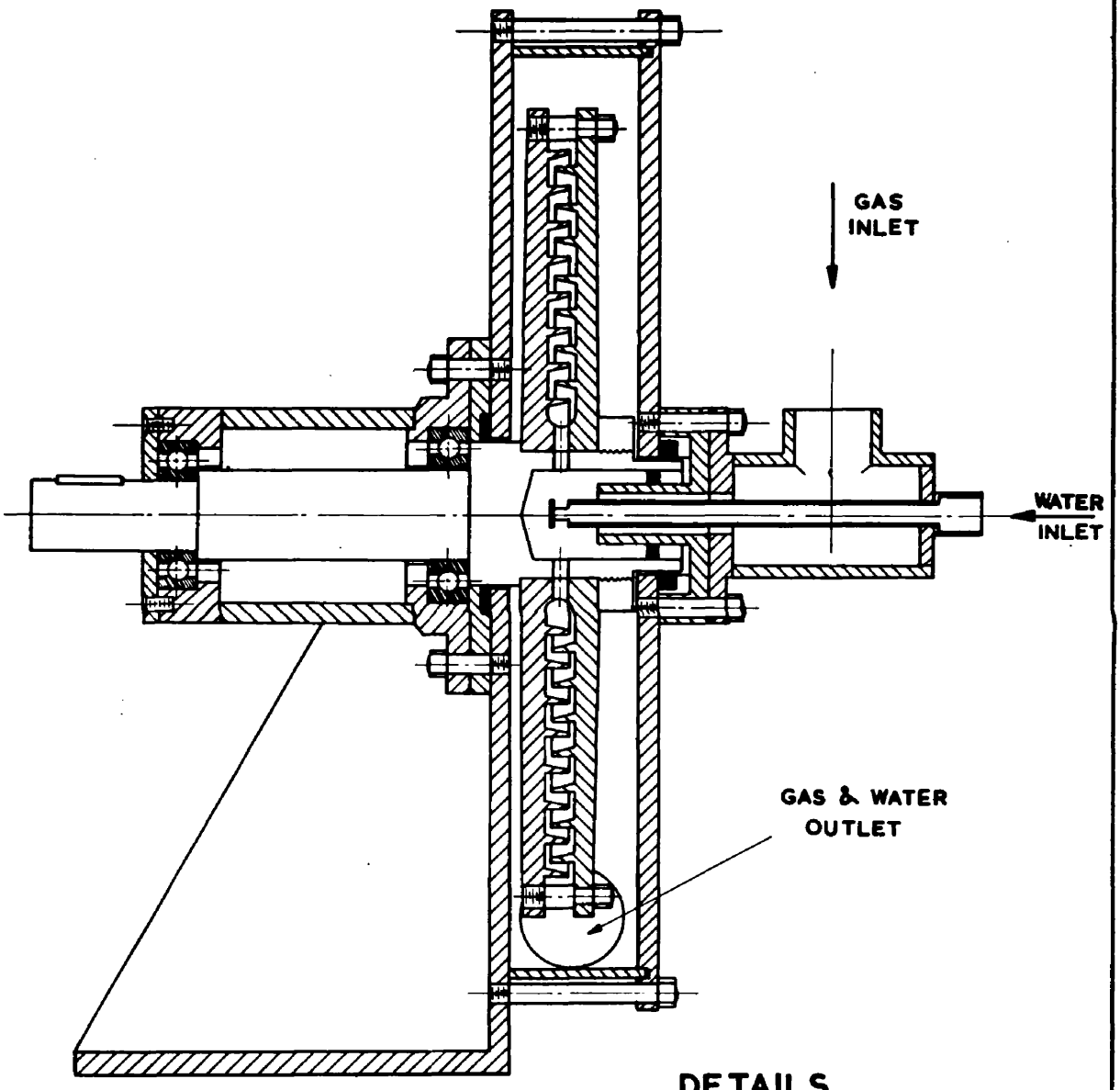
τ = Constant related to rate of penetration of liquid film by the zone of rapid chemical reaction.

SECTION I

INTRODUCTION

It is predicted by the penetration theory of gas absorption, as developed by Higbie[4] and Danckwerts[5], that absorption rates at freshly formed liquid surfaces will be high. Work on liquid jets[49] substantiated this prediction and led to the design of an absorber[61] in which very high absorption rates would be possible through the rapid formation of fresh liquid surfaces. The basis of design was the high speed rotor stillhead of Piazza[62] and the Podbielniak fluid contractor[63] in which the gas and liquid phases moved simultaneously with intimate contact. The form of the rotor is shown in Fig. 7. It has two fixed plates each with a number of concentric rings which are designed, when rotating, to accelerate the liquid phase by centrifugal force and throw it outward through the gas phase. At each ring the liquid droplets collect and are redistributed thus ensuring frequent renewal of the ageing surfaces. The actual liquid distribution in centrifugal absorbers was investigated by Dixon[64] who photographed spray patterns through a perspex rotor-stator form of the absorber. No work is reported on

spray/



DETAILS
OF
CENTRIFUGAL ABSORBER

FIG. 7

spray formation in the double rotor form.

The present work consists of investigation in to the absorption characteristics of the physical absorption systems, carbon dioxide-water, ammonia-water, methanol-water, methyl acetate-water, and acetone-water with particular reference to the comparison of liquid and gas film effects in such absorbers. Previous papers on the performance of centrifugal absorbers have dealt with systems in which chemical reaction accompanies the absorption processes, viz., carbon dioxide-monoethanolamine[65] and carbon dioxide-ammonium hydroxide[61]. Both systems show results indicating large absorption rates as compared with other types of absorption apparatus.

EXPERIMENTAL

Details of the centrifugal absorber are given in Fig. 7. It has a horizontal axis with a 12" O.D. rotor keyed on to a 2½" D. hollow spindle. Six 1/4" D. holes are bored radially through the spindle and absorber hub to allow the gas and water to enter the absorption chamber. The previous design of gas-liquid entry permitted the gas and liquid to mix at a point outside the actual hub and, although it was considered/

considered impractical to construct entirely separate inlets, the modified form gave much less contact before the rotor proper.

The rings on each plate meshed alternately; the first ring was of 4" O.D. and succeeding rings were set at ½" increase in diameter. The plates were ½" apart and the rings were 3/8" deep and tapered from 3/16" at the base to 1/16" at the apex. There were three such rotors, No. 1 had plain rings, No. 2 had alternate rings drilled 1/16" D. at 1/8" pitch and No. 3 had slots 0.04" in width and 1/16" deep at 1/8" centres cut in alternate rings. The absorption space between the plates had a volume of 0.033 ft^3 and the block volume of the absorber was 0.062 ft^3. The absorber rotor was driven by a 2 H.P. electric motor through a double set of V belt pulleys to allow for speed variation.

A diagram of the plant is shown in Fig. 8. Water from an overhead storage tank was pumped by a variable speed gear pump to the absorber hub. A rotameter indicated the flow rate. Pure gas, in the case of the ammonia and carbon dioxide, was throttled from 28 lb. bottles of the liquified gas and diluted as required by air from a rotary vane blower/

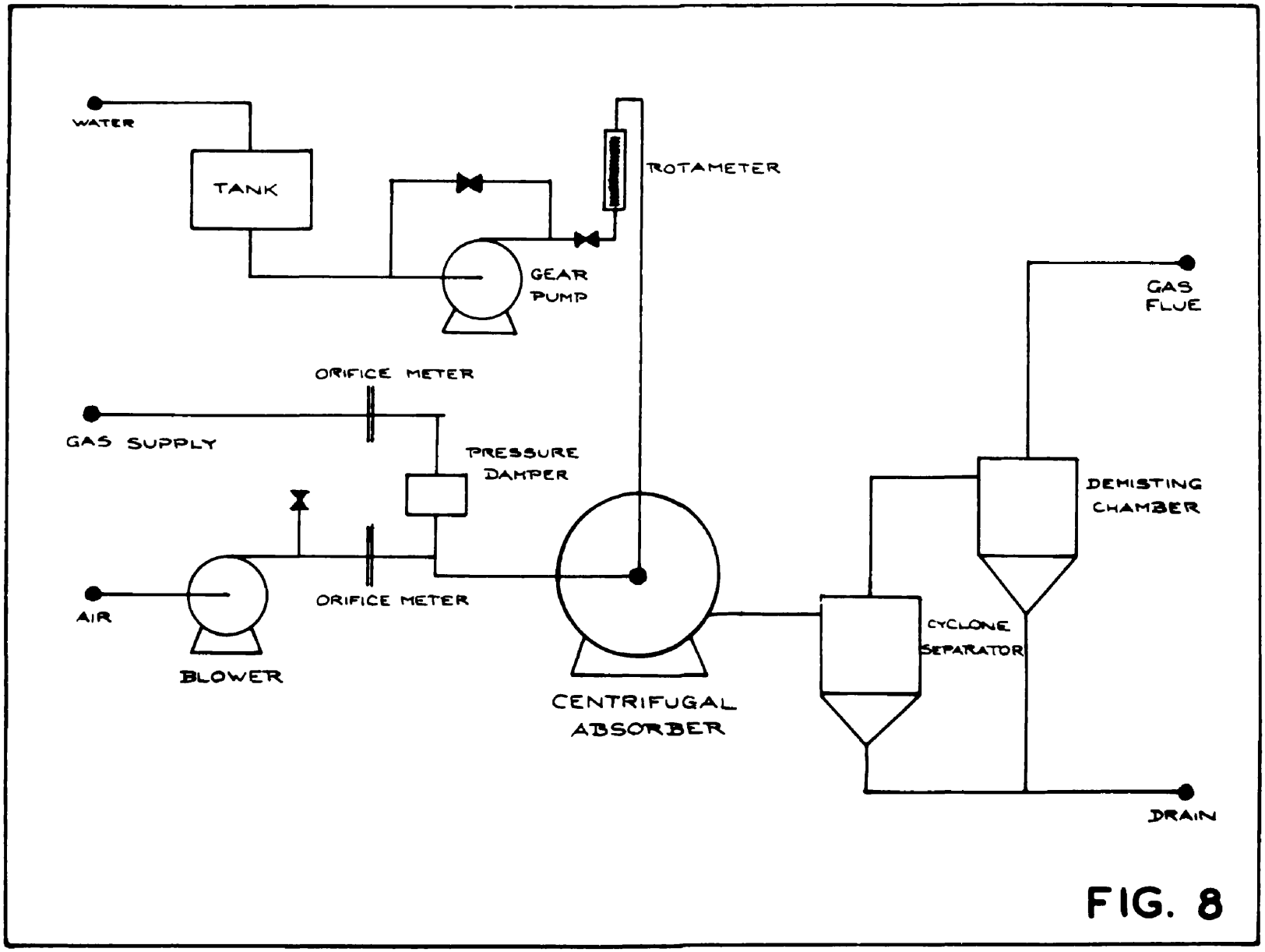

WATER
TANK
ROTAMETER
GEAR PUMP
GAS FLUE
ORIFICE METER
GAS SUPPLY
PRESSURE DAMPER
DEMISTING CHAMBER
AIR
ORIFICE METER
CYCLONE SEPARATOR
BLOWER
CENTRIFUGAL ABSORBER
DRAIN

FIG. 8

blower capable of delivering about 1200 ft^3/hour of air at the plant inlet working pressure. The flow rate in both air and gas lines was calculated from orifice plate readings. The effluent from the absorber flows through a single pipe into a cyclone separator. The gas blows through a final cyclone demister before leaving to atmosphere. The organic vapours were formed in a vapourizer consisting of a steam jacketed brass tube 12' x 1" O.D. x 1/16" wall. Liquid was fed in to the vapourizer from a calibrated reservoir by means of a centrifugal pump with an adjustable by pass. All pipe work from entry of vapour to the absorber hub was lagged with asbestos rope as a precaution against condensation, although the working conditions were well below saturation values of the air stream. Temperature and pressure measurements were made where ever required.

The amount absorbed was estimated by analysis of the outlet liquid in each case. Estimation of carbon dioxide in water was made by a method described by McKinney and Amorosi[66]. Ordinary acidmetric titrations sufficed for ammonia estimation while the acetone estimations were made by addition of

hydroxylamine/

hydroxylamine hydrochloride and titration of the free acid produced. The methyl acetate content of the water was determined by hydrolsis with excess NaOH solution and back titration, while the methanol analysis was obtained from specific gravity measurements of a water sample distillate.

Gas analyses were direct in the case of carbon dioxide and the various organic vapours. These latter were burned over a platinum wire and the resulting carbon dioxide estimated in a Sleigh Analysis unit. The ammonia was estimated by absorption in standard acid. Two ordinary wash bottles gave apparently complete recovery. In the final assessment of results, tests which failed to give a satisfactory mass balance were rejected. It was estimated that concentrations of acetone, etc., in the exit gas stream could be measured with an accuracy of 1 part in 10,000 (by volume), while the estimation of ammonia and of carbon dioxide was not less than 1 part in 1,000. A good mass balance, therefore, should certainly be to within $\pm$ 1%. but a reasonable experimental accuracy of $\pm$ 5% was adopted as a standard.

In this connection it might be noted that a rotary multi/

multi blade blower used for air supply set up a stationery pressure wave in the orifice of the gas supply line and introduced a troublesome discrepancy in mass balance which took some time to detect and eliminate. The cure was found in the introduction of a pressure damping reservoir, as shown in Fig. 8, between the air and gas lines.

The principal analytical problem laid in the very close approach to equilibrium set up by the washer in the outlet gas-liquor mixture. Data on the systems for ammonia-water, acetone-water and the like are not very complete or exact, especially at low partial pressures for the solutes. Only careful temperature determination in a fast moving fluid stream, with considerable extrapolation of equilibrium curves, allowed any estimate of partial pressure difference to be made at all. In these circumstances it was decided initially to express all results in the form of lb.moles absorbed per cubic foot of absorber volume per hour (N_a) rather than in the normal form of lb.moles/ft^3/hr/atm. In order to conform with the ammonia, methanol, methyl acetate and acetone results, the figures for carbon dioxide are put in the same form, although the slower absorption/

absorption of this gas allowed a more accurate estimation of concentration head to be made.

RESULTS

Pressure drop across absorber

Preliminary tests were carried out to establish the effect of water, gas rate, and rotor speed on the pressure drop across the washer. It was found, as shown in Fig. 9, that up to 1,500 lb./hr. the water rate was directly proportional to the pressure drop. Above this rate the water tended to form seals in other parts of the plant which increased the total load on the gas blower above its rating. Gas rates fell off and the system became unstable. Similar phenomena occured when the gas rate (Fig. 10) was increased above 1,400 ft^3/hr. Up to this point the pressure drop increased steadily with gas velocity. Somewhat surprisingly (Fig. 9) the rotor speed could be varied from 680 to 3,120 r.p.m. with no obvious effect on the pressure drop. In essence the rotor forms a crude centrifugal exhauster, with a peripheral speed of up to 157 ft./sec. at 3,000 r.p.m., corresponding to/

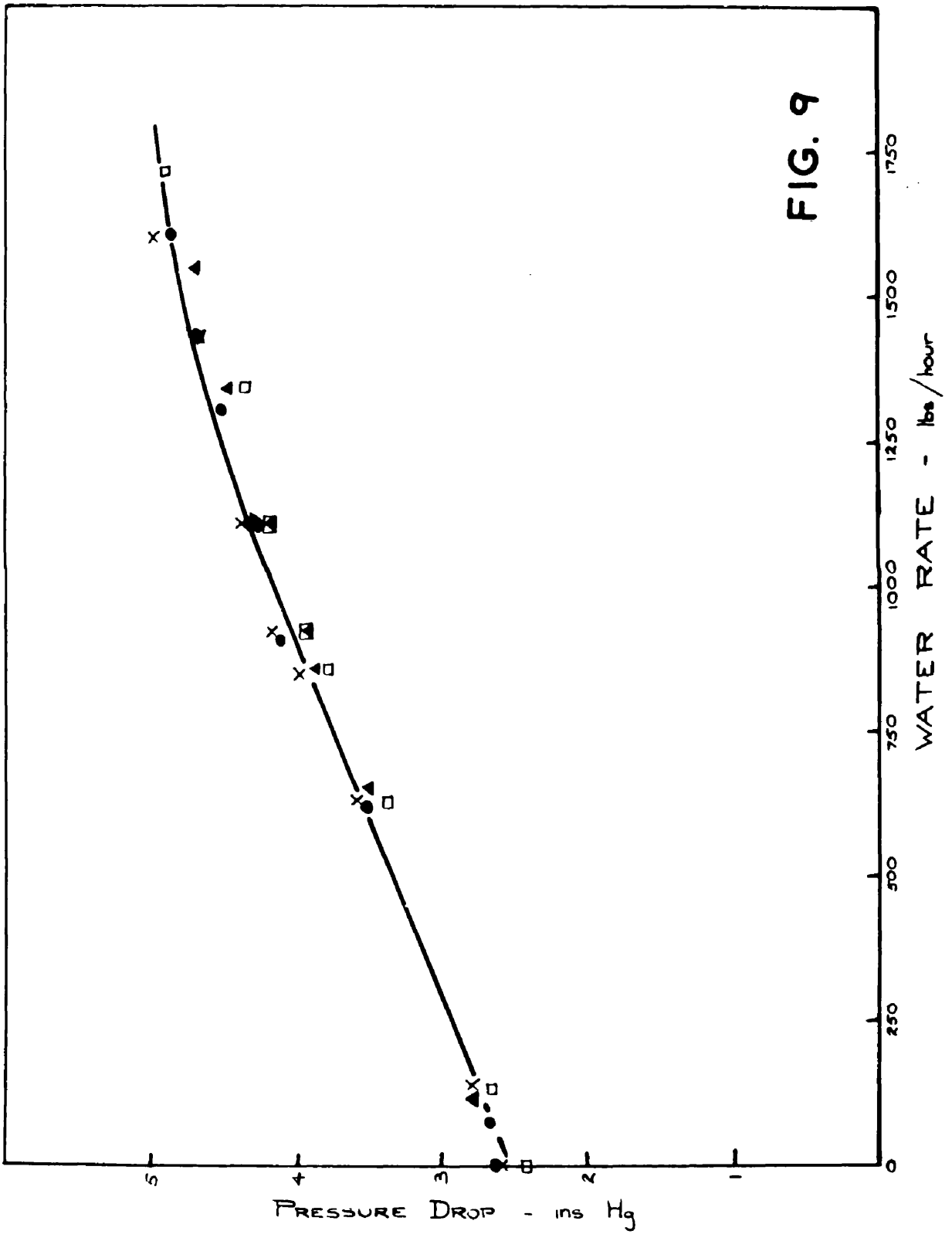


FIG. 9
WATER RATE - lbs/hour
0
250
500
750
1000
1250
1500
1750
PRESSURE DROP - ins Hg
5
4
3
2
1

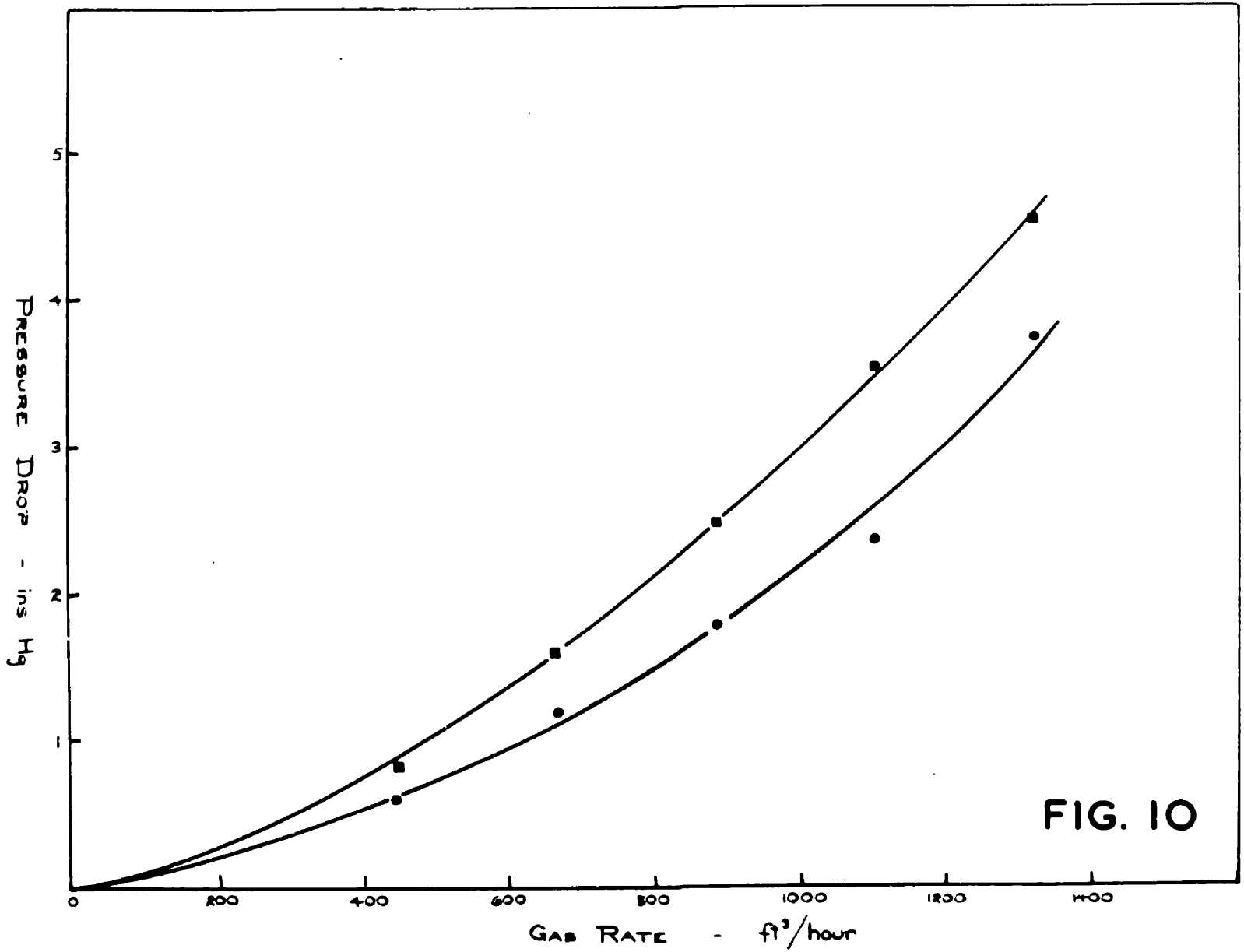

Pressure Drop - ins Hg
5
4
3
2
1
0
200
400
600
800
1000
1200
1400
Gas Rate - ft³/hour

FIG. 10

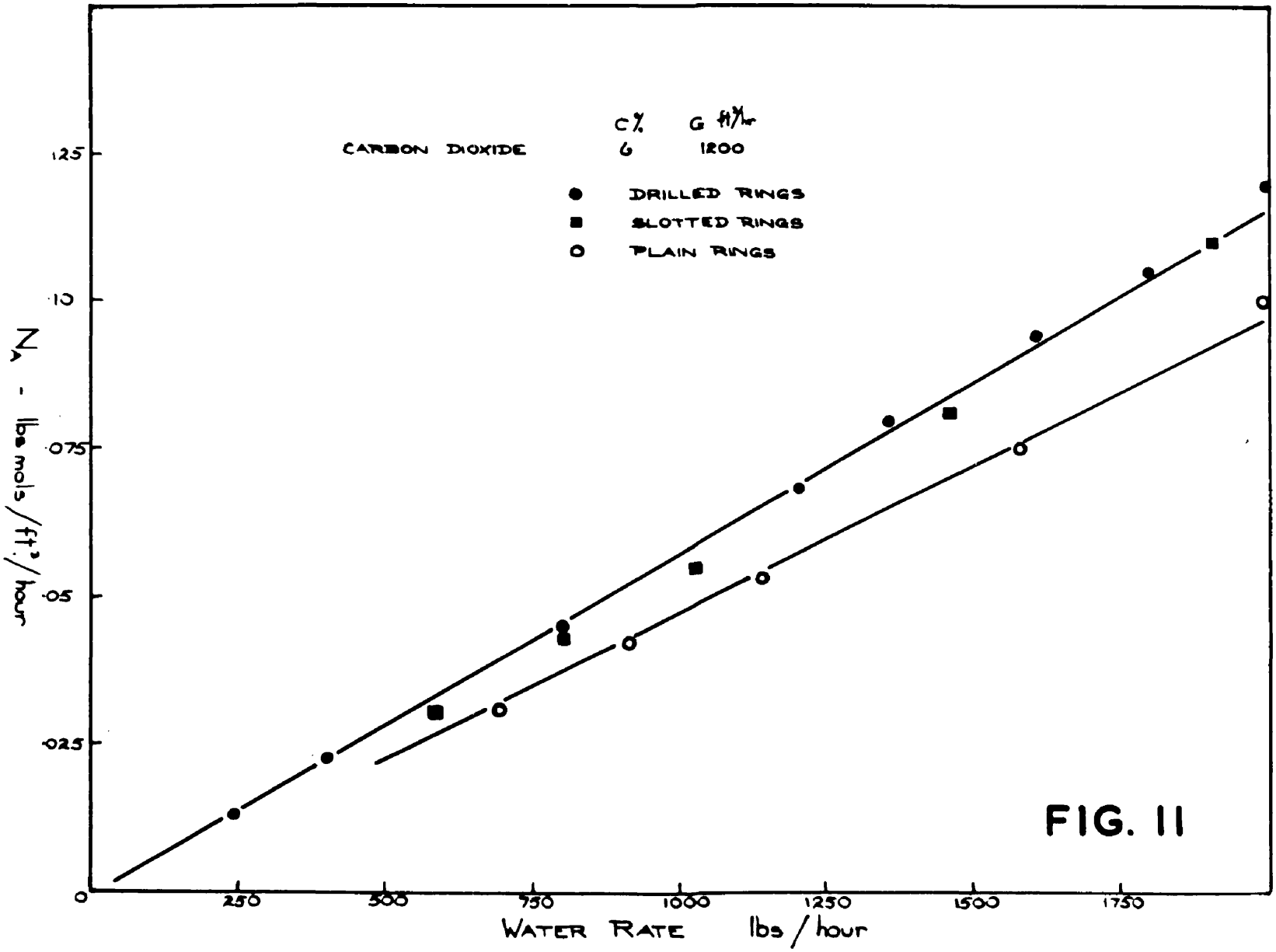

CARBON DIOXIDE
C%
G #/hr
6
1200
DRILLED RINGS
SLOTTED RINGS
PLAIN RINGS
N_A - lbs mols/ft²/hour
.125
.10
.075
.05
.025
0
250
500
750
1000
1250
1500
1750
WATER RATE lbs / hour

FIG. 11

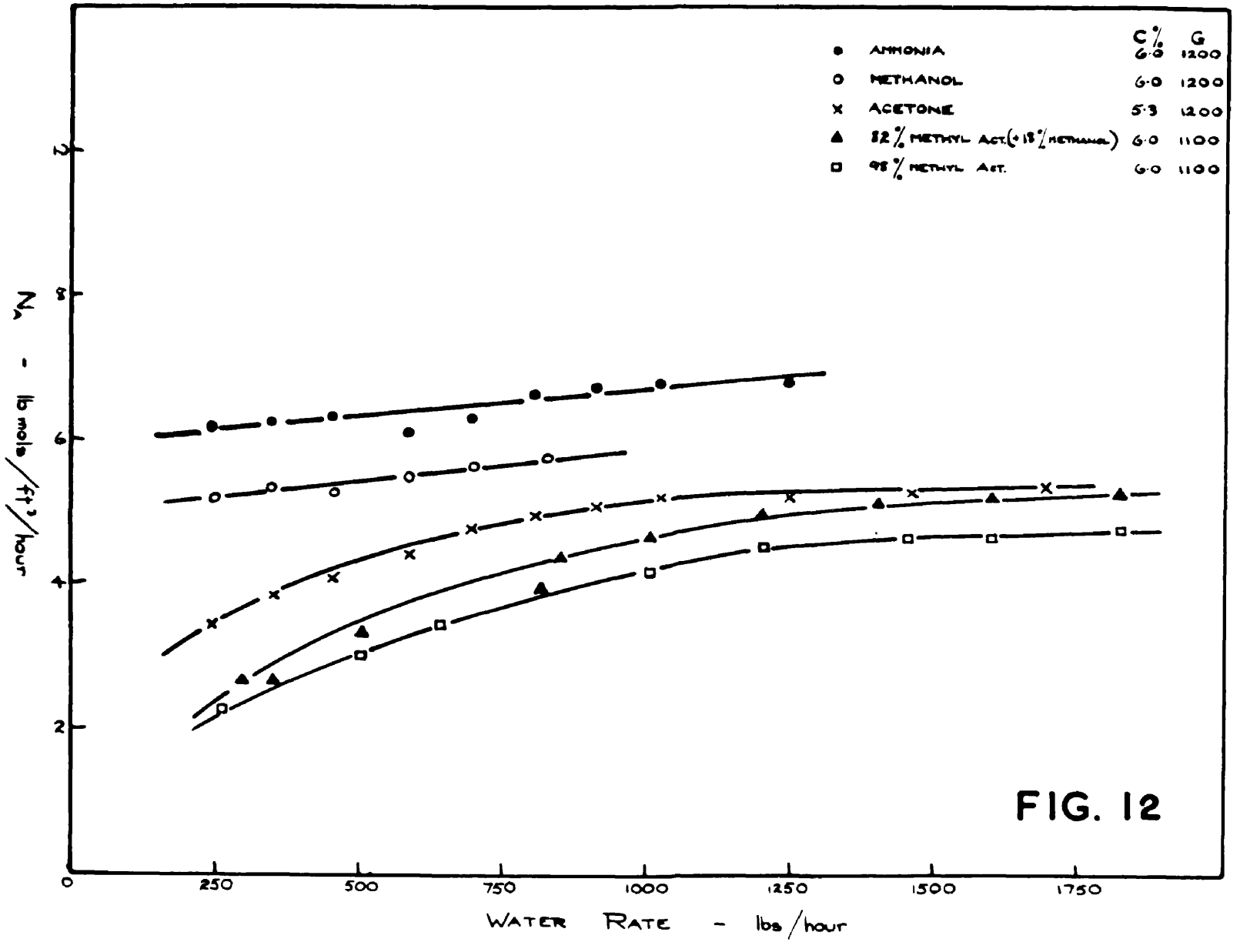

C% G
AMMONIA 6·0 1200
METHANOL 6·0 1200
ACETONE 5·3 1200
82% METHYL ACT.(18% METHANOL) 6·0 1100
98% METHYL ACT. 6·0 1100
N_A - lb mole/ft²/hour
0
2
4
6
8
250
500
750
1000
1250
1500
1750
WATER RATE - lbs/hour

FIG. 12

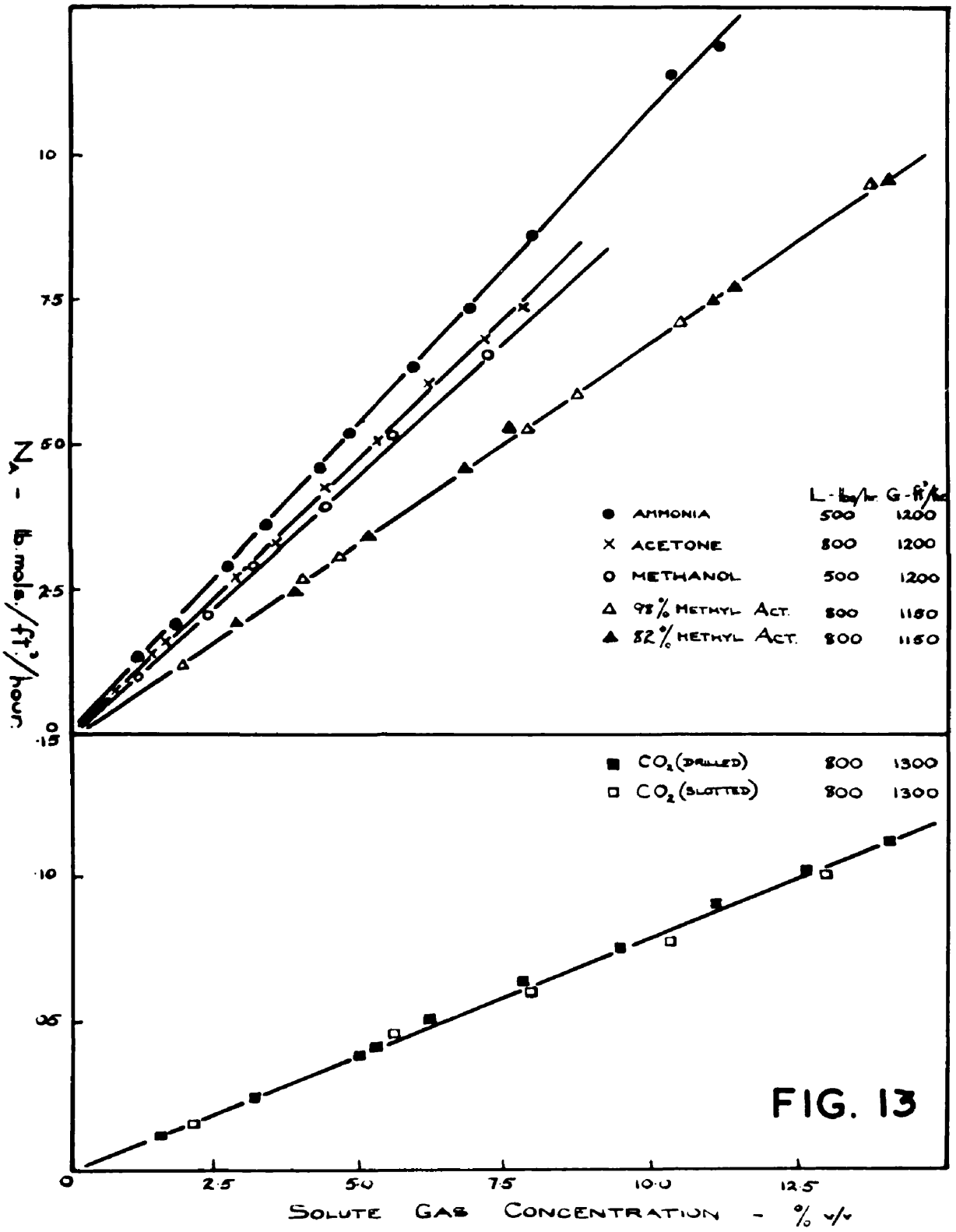

N_A - lb.moles/ft.²/hour
10
7.5
5.0
2.5
1.0
.15
.10
.05
0
2.5
5.0
7.5
10.0
12.5
SOLUTE GAS CONCENTRATION - % v/v
L - lbs/hr. G - ft³/hr
● AMMONIA 500 1200
× ACETONE 800 1200
○ METHANOL 500 1200
△ 98% METHYL ACT. 800 1150
▲ 82% METHYL ACT. 800 1150
■ CO_2 (DRILLED) 800 1300
□ CO_2 (SLOTTED) 800 1300

FIG. 13

to a potential pressure of 5 - 6 inches of water gauge at the outlet (air basis). This will be considered later.

Effect of water rate on absorption rates

Fig. 11 shows that the absorption rate of carbon dioxide increases linearly with water rate. The equation of the line marked at the bottom of the chart is given by

$$N_a = 5.7 \times 10^{-5} L \qquad (57)$$

where L is the liquid rate in lbs./hour.

The effect of different ring contours is very small - at any rate for the carbon dioxide-water system - as will be seen by the lower line in Fig. 11. While all results with slotted or drilled rings are slightly higher than with a plain ring, the change is unimportant - almost within experimental error range. There was evidence in the form of slight erosion marks to show that the liquid had flowed through the openings in the rings, but clearly no marked change in liquid dispersion had occured.

In experiments with ammonia and methanol (Fig. 12) the outlet streams had to all intents and purposes reached/

reached complete equilibrium. Within the range of concentrations used this involved an equally complete removal of solute from the gas phase, with consequent analysis difficulties. On the other hand methyl acetate and acetone did show more variation with water rates and a slower approach to equilibrium (Fig. 12). The lower solubility of methyl acetate in water vis a vis ammonia and methanol would perhaps explain the change here, and the effect can be traced in the case of acetone.

Effect of gas concentration on absorption rates

In each of the systems investigated increase of solute concentration in the inlet gas produced a corresponding linear increase in absorption rate as seen from Fig. 13. This would be expected in view of the high percentage absorption of all solutes - even the methyl acetate. The most easily measured carbon dioxide had a straight line relation (Fig. 13) with an equation

$$N_a = 7.6 \times 10^{-3} C_g \qquad (58)$$

where C_g is the % of carbon dioxide in the inlet gas.

Effect/

Effect of rotor speed on absorption rate

From Table I it is seen that an increase in rotor speed gave a slight decrease in the absorption rate of carbon dioxide into water. The results for acetone, methanol and methyl acetate and ammonia show no change as the rotor speed varied from 680 - 3120 r.p.m.

TABLE I

System	Water Rate	Gas Conc.	N_R(680 r.p.m.)	N_R(1120 r.p.m.)	N_R(1880 r.p.m.)	N_R(3120 r.p.m.)
CO_2	800	5.0	.0392	.0370	.0350	.0330
CO_2	1600	5.0	.0775	.0690	.0651	.0651
NH_3	500	5.9	6.24	6.42	6.28	6.34
CH_3OH	500	5.0	3.55	3.87	4.00	3.74
CH_3COOCH_3	500	6.0	4.30	4.00	4.20	4.20
C_3H_6O	800	5.3	5.08	5.12	5.22	5.15
C_3H_6O	525	5.3	4.48	4.39	4.64	4.48

G - 1300 $ft^3/hr.$

Effect of gas velocity on absorption

Over the range covered, the absorption rate of carbon dioxide into water was almost unaffected by variation in gas flow. The methyl acetate results show that increase in gas velocity produces increase in absorption rates over the range 600 - 1200 $ft^3/hr.$ Higher/

Higher rates were not investigated because of the high velocity heads produced at the restricted gas entry to the absorber. The range covered is hardly broad enough to warrant any definite conclusions on this factor. Results are set out in Table II.

TABLE II

	Carbon Dioxide		Methyl Acetate	
	Water Rate		Water Rate	
Gas Rate ft^3/hour	80 Gals/ hour	160 Gals/ hour	50 Gals/ hour	100 Gals/ hour
660	.0572	1.020	2.56	2.62
880	.0572	1.085	2.77	3.80
1100	.0572	1.150	3.21	4.35
1320	.0572	1.210	3.87	4.41

Effect of methanol on the absorption of methyl acetate in water

From Fig. 12 it can be seen that there is a slight increase in absorption rates when methanol is present in the gas phase. This is presumably a result of the increase om surface area presented to the gas by the decrease in surface tension of the liquid due to presence of methanol. It may be assumed that the presence of methanol at the interface does not interfere with the absorption process.

DISCUSSION

Rotor Speed

When gas and liquid are forced into the centre of a rotor which is spinning at high speeds they will move in accordance with the centrifugal forces and the flow at entrance. In a typical case, the gas (1200 ft^3/hr.) and the liquid (1600 lbs./hr.) are forced in at a rate which will give a contact time of about 0.1 sec. in a stationary rotor. A 12" diameter rotor having a speed of 1000 r.p.m. will exert a maximum centrifugal acceleration outwards of 550 ft./sec^2., sufficient to move a unit particle of fluid from centre to rim in about $^1/_{74}$ sec. This indicates that the effect of centrifugal force was the factor controlling the time of contact and the centrifugal effect gives contact times which are inversely proportional to the speed of the rotor in r.p.m. Some absorption must take place during the initial mixing in the entrance tube, and also in the disengaging space of the rotor casing. It will be assumed that these effects are relatively small compared with the intensive mixing in the actual rotor. The system thus reduces to a parallel (non-mixing) flow channel for two phases, with a short zone of intense mixing. If the intensity of mixing is increased and the zone reduced, the results of mixing/

mixing can remain the same, or where I is the mixing intensity and T is the mixing time (I x T) is constant.

Pressure Drop

In as much as the rotor formed a centrifugal exhauster or pump it would be expected that the pressure drop over the entire washing unit would diminish as the rotor speed increased. Assuming that the mixture set out above behaved as a fluid of mean density 1.4 lbs./ft.^{3} it would develop pressures up to 0.4 lbs./in.^{2} in the conditions specified. Now the smallest pressure drop observed with no water flowing, was about 1.2 lbs./in.^{2} and, at the water rate for mixture densities of 1.4 lbs./ft.^{3}, was 2.14 lbs./in.^{2} Bearing in mind that the actual pressure developed by centrifugal action might be less than half the theoretical maximum, or 0.2 lbs./in.^{2} (0.4 in water), it is not surprising that the effects of centrifugal pumping on pressure drop are hard to discern (Fig. 9).

It may be assumedthat pressure drop is caused largely by the small area available for liquid and gas flow im the entrance passages and the innermost ring system.. The total area for passage into the rotor proper consists of six holes, each $^1/_4$ in. in diameter, or/

or a total of 3.4×10^{-3} ft^2. Velocity through these passages is of the order of 100 ft./sec., giving a velocity head of 1.5 lbs./in^2. While much of this may be recovered in the system, the calculation shows that a large proportion of the back pressure is developed in the entry section. Doubt will always exist as to the amount of solute absorbed in this section.

Absorption Rates

For ammonia and methanol and to a lesser extent for acetone and methyl acetate, the effect of water rate on absorption was masked by the almost complete absorption obtained. At all rates of water flow above 1000 lbs./hr. the removal of solute was so complete that the two phases were in almost complete equilibrium, and no reliable determination of partial pressure difference could be made. For purposes of measurement, conditions were more satisfactory in the water-carbon dioxide system. It was not found possible to arrange for anything more than traces of ammonia or methanol to appear in the outlet gas stream without deviating widely from normal operating conditions. When using acetone and methyl acetate, certain low water rates did give more measurable concentrations/

concentrations in the outlet gas.

With carbon dioxide, a steady increase in the amount absorbed showed that water rates determined the rate of absorption almost completely. By contrast, increase in gas rate gave little or no change. This is in accordance with results previously reported and indicated that absorption of carbon dioxide is controlled by water film conditions. In the inter: :mediate cases of acetone and methyl acetate, the amount absorbed increases with water rates up to a value of about 1000 lbs./hr. and this is followed by conditions similar to those for ammonia and methanol, in that almost all the solute entering is removed.

The five sets of results can be related as shown in Fig. 14 in which the amount of solute removed is plotted against liquid on an adjusted scale to show the differences in solubility. In the case of ammonia and methanol on the right of the diagram, it is probable that the liquid surface film was never fully saturated at any time, rapid diffusion due to their high solubility removing the gases as soon as they came in contact with the liquid. With carbon dioxide, on the left, the surface film was fully saturated as it formed, and the

working/

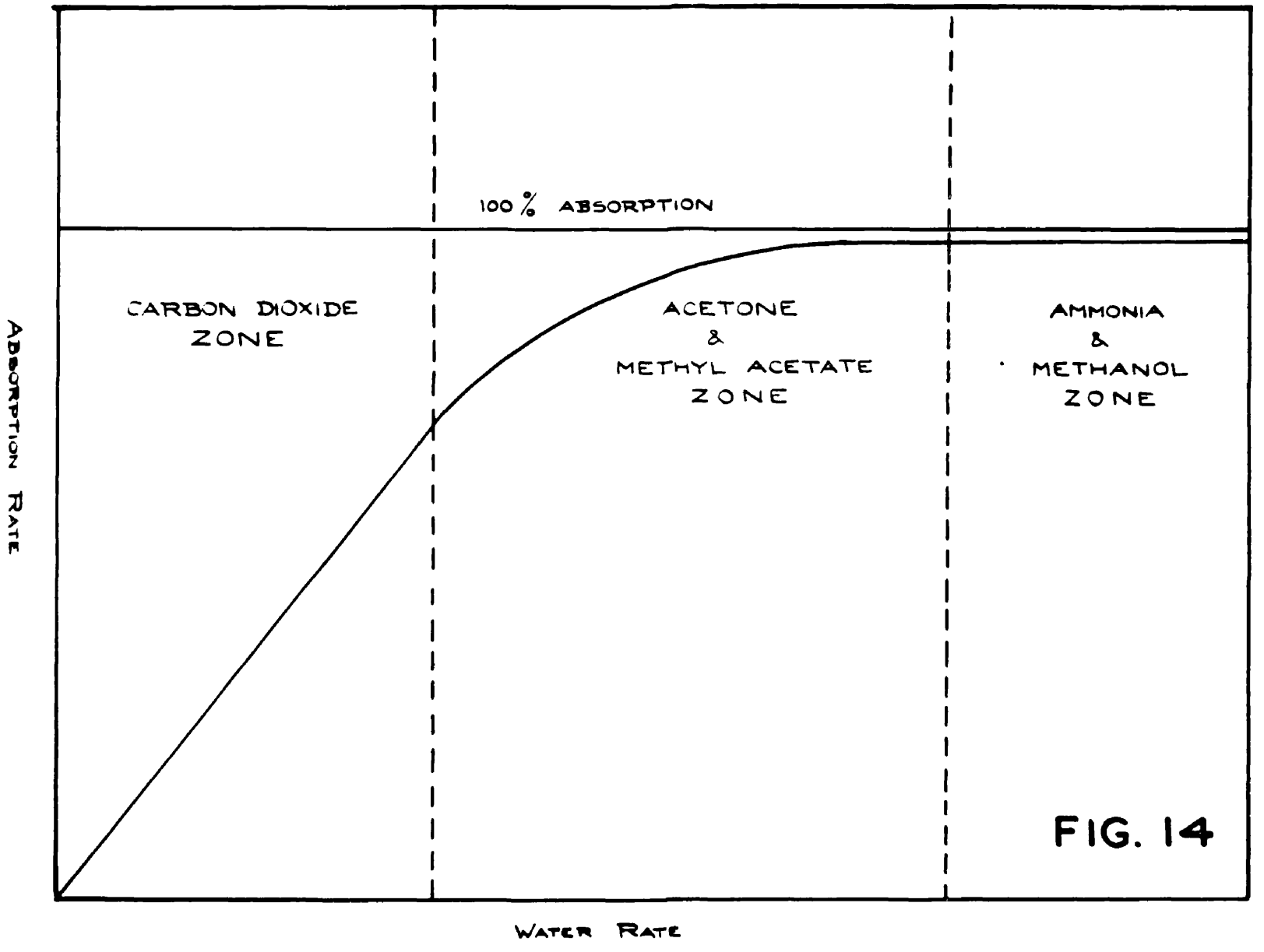

100 % ABSORPTION
CARBON DIOXIDE ZONE
ACETONE & METHYL ACETATE ZONE
AMMONIA & METHANOL ZONE
ABSORPTION RATE
WATER RATE

FIG. 14

working of the rotor allowed an increase of surface with increase in water rate. Acetone and methyl acetate showed the characteristics of an intermediate system, with unsaturated surface on the right and a fully saturated on the left.

The results, however, may be analysed more fully on the concept of a transfer unit. Assuming that the centrifugal unit corresponds to a total volume V, through which flow a gas (G_m moles) and liquid (L_m moles) pass in concurrent flow, then in a section of volume cV, adopting normal nomenclature

$$-G_m dy = L_m dx = k_L a(c_e - c_l)dV$$

Where the average molal density of the liquid is C, the $c_e/C = x_e$ etc. and

$$L_m dx = k_L a.C.dV(x_e - x_l)$$

whence by arrangement and integration

$$\int_{x_1}^{x_2} dx/(x_e - x_l) = (V.C.k_L a)/L_m = N_L$$

where N_L is the number of liquid film transfer units involved.

Then V/N_L = the "volume of a liquid film transfer unit"/

unit" = $L_m/(C.k_La)$. An alternative construction gives the "volume of a gas film transfer unit" as $G_m/(P.k_Ga)$. This "volume of a liquid film transfer unit" is denominated as VTU_l. Using a similar analysis the "volume of a transfer unit" (overall liquid basis), or VTU_{ol} is given by

$$V.T.U._{OL} = L_m/(C.k_La) = (L_m/C)(1/k_La + \frac{1}{H.k_Ga})$$

where H is Henry's Law Constant

$$p_e = H.c_e$$

Then,

$$V.T.U._{OL} = V.T.U._L + L_m/H.C.k_Ga$$

$$= V.T.U._L + (L_m/G_m)(P/H.C.)(G_m/P.k_Ga)$$

$$= V.T.U._L + (L_m/G_m.m)(V.T.U._G)$$

where m has the composite value of H.C./P

A measure of the respective values of the film transfer unit can be obtained by plotting VTU_{OL} against

$$L_m/(G_m.m),$$

or VTU_{OG} against $(m.G_m)/L_m$. Then VTU_{OL} approximates to VTU_L as $L_m/(G_m.m)$ tends towards zero, and VTU_{OG} approximates to VTU_G as $(m.G_m)/L_m$ diminishes.

Only/

Only the figures for carbon dioxide are really reliable, and they are the only set analysed fully on these lines. There is a possible basis for comparison under standard conditions with all five solutes. If it is assumed that 99% of saturation is reached with methanol, acetone, methyl acetate and ammonia, using 800 lbs./hr. of water and 1320 ft^3/hr. of gas, then the values of VTU_{OG} and VTU_{OL} are as set down in Table III.

TABLE III

Gas	$V.T.U._{OG}$	$V.T.U._{OL}$	$L_m/m.G_m$	$m.G_m/L_m$
Carbon Dioxide	4.7	0.04	0.0087	115.0
Methyl Acetate	0.0012	0.044	3.03	0.33
Acetone	0.0077	0.06	7.25	0.14
Ammonia	0.0065	0.11	16.5	0.06
Methanol	0.00675	0.45	74.5	0.0134

From the general equation

$$VTU_{OL} = VTU_L + (L_m/G_m.m)(VTU_G),$$

it will be seen that liquid film conditions control absorption with carbon dioxide ($VTU_{OL} = VTU_L$) except for very abnormal gas conditions. On the other hand as

$$VTU_{OG} = VTU_G + (G_m m/L_m).(VTU_L)$$

it is probable that liquid film resistances are of negligible/

negligible importance in the absorption of ammonia and methanol, but slightly more effective with acetone and methyl acetate.

The results of varying liquid and gas rates are set out in Table IV, and a graph of VTU_{OG} against I/L_m (Fig. 15) shows

TABLE IV

L_m	G_m	N_{OL}	N_{OG}	V.T.U.$_{OL}$	V.T.U.$_{OG}$
22.2	3.66	0.825	0.00352	0.04	9.4
44.4	3.66	0.825	0.00704	0.04	4.68
66.6	3.66	0.825	0.01056	0.04	3.12
88.8	3.66	0.850	0.01450	0.039	2.28
111.0	3.66	0.870	0.01850	0.038	1.79
44.4	1.83	0.56	0.0095	0.059	3.48
44.4	2.45	0.56	0.0072	0.059	4.60
44.4	3.06	0.56	0.00575	0.059	5.75
44.4	3.66	0.56	0.0048	0.059	6.89

that VTU_G approximates to zero, a result substantiated by the constant value for VTU_{OL} when the gas rate is varied. The two characteristic equations reduce to

$$VTU_{OL} = VTU_L$$

and

$$VTU_{OG} = (G_m m/L_m)(VTU_L)$$

It has been shown that $VTU_L = L_m/C.k_L a$ and the constancy/

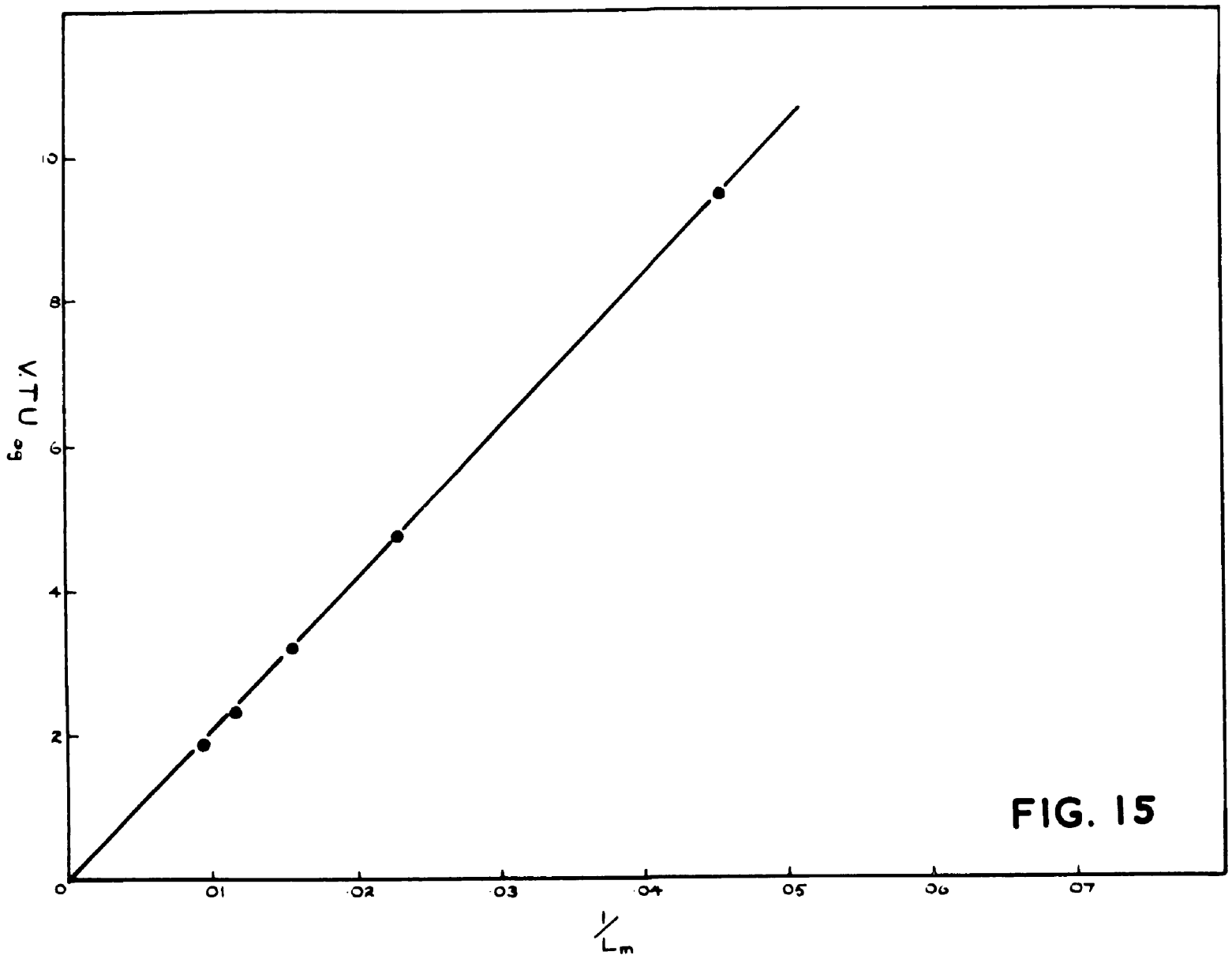


FIG. 15

constancy of the value for VTU_{OL} as the liquid rate varies (Table IV) suggests that k_La varies directly as L_m, the liquid rate. However, the true time of contact is proportional to neither liquid rate not to gas rate, but to the rotational speed of the washer. Similarly the degree of turbulence is determined by centrifugal flow, impact, and redistribution of both phases. These again are relatively uninfluenced by the actual rate at which the two fluids enter. Thus it may be supposed that water entering the washer is transformed into a certain area of carbon dioxide accepting surface, this surface area being proportional to the weight of water present and to the degree of turbulence - measured by the centrifugal effect or speed of rotation of the washer.

At constant speed, therefore, a fixed weight of water appears to provide a certain area of absorbing surface. For carbon dioxide, this area is proportional to the weight of water passing. Hence doubling the water rate doubles the surface available and hence the absorption. The value of $dx(x_e - x_1)$ is constant, as demonstrated experimentally. The time of contact and degree of dispersion or mixing appear to be inverse variables, determined/

determined by the rotor speed, and being independent of the rates of gas and liquid flow. As the dispersion is effectively doubled, the time of contact is halved by the same increase in rotor speed.

The water provides an accepting area for the solute, and according to the measurements made with carbon dioxide, this area is directly proportional to the amount of water flowing. In this instance, however, the surface may be taken as fully saturated by the absorbed gas, and further absorption is controlled either by steady diffusion through a static film (Whitman's Two Film Theory) or by specific surface renewal (Higbie- Danckwerts). Increase in the rate of flow of water can be considered to provide either thinner films due to greater turbulence or provide more frequent surface renewal, according to the theory adopted.

When ammonia and methanol are being absorbed, migration into the body of the liquid from the surface is very much faster and, in fact, the surface may never become saturated. The rate of migration of gaseous ammonia and methanol to the liquid surface is controlled by gas film conditions, and will normally make/

make for much more rapid absorption than in liquid film controlled absorptions. Whatever the amount of water flowing, it is amply sufficient to give almost complete equilibrium in the washer. In the case of acetone and methyl acetate, low water rates appear to give a fully saturated surface and a measure of liquid film control. As the water rate is increased, the absorbing area formed is so large that saturation conditions are not reached, and the rapid absorption rates characteristic of gas film control are again obtained. Such an explanation suggests poor distribution with small quantities of water (films of the order of 1/1000th of an inch are calculated to exist at the outer rings), and the centrifugal washer may be compared to a packed tower with unevenly wetted packing.

If the "two film" theory of gas absorption is accepted it would appear (Table I) that the gas film and the liquid film are equally affected by an increase in centrifugal velocity. In fact the small but definite fall in carbon dioxide absorption as rotor speed increases suggests that the liquid film conditions are not so closely/

closely tied to rotor speed as are the "two film" systems of acetone-water, ammonia-water, methanol-water and methyl acetate-water, where absorption rates are constant.

But it would be equally true to explain the results as due to a liquid surface absorption which was complete with carbon dioxide, complete at low water rates with acetone and methyl acetate, and never fully complete with ammonia and methanol. Renewal of the surface by centrifugal action is insufficient at high rotor speeds for carbon dioxide to be absorbed in the shorter time available. When the organic vapours or ammonia are being absorbed the renewal is sufficiently fast to balance the shorter time; some diminution of surface tension may also occur here.

In the circumstances, therefore, no definite choice can be made between the classical "two film" theory and the penetration theory.

A list has been drawn up of the various systems investigated (Table V) with the value (column 5) of $K_g a$, based on the most reasonable experimental figures, with the relative diffusion coefficients in water and air (columns 2 and 3) and the relative slopes of the equilibrium/

equilibrium line (column 4).

Goodgame and Sherwood[30] have suggested a formula for $K_G a$ based on actual measurements for carbon dioxide absorption and water vapourisation - $k_L a$ and $k_G a$ respectively in an ideal system. They propose that these values be transformed into other systems by multiplying with the square root of the Diffusion Coefficient ratio thus

$$\frac{1}{K_G a} = \frac{1}{k_G a \left(\frac{D_v}{D_{vH_2O}}\right)^{0.5}} + \frac{1}{k_L a \left(\frac{D_L}{D_{LCO_2}}\right)^{0.5}} \quad \text{---- (56a)}$$

Values for $K_G a$ based on this formula have been calculated and are shown in Column 7.

Again if the Higbie-Danckwerts mechanism of surface renewal is accepted, then for all these figures the rate of renewal is the same but the overall values for $K_G a$ would be proportional to the square root of the controlling diffusion coefficient(s). Taking the carbon dioxide values as established, relative values for the other system have been calculated and are shown in Column 6.

TABLE V

TABLE V

System	D_L (ft^2/hr) x 10^5	D_V (ft^2/hr)	H (atm/(lb mol/ft^3))	K_Ga(1)	K_Ga(2)	K_Ga(3)
Methanol-Water	4.9	.515	.049	535	5250	920
Ammonia-Water	6.8	.836	.215	545	1400	660
Acetone-Water	3.2	.350	,460	468	460	370
Methyl Acetate -Water	2.9	.326	1.16	300	170	190
Carbon Dioxide -Water	5.8	.535	408	.77	.77	.77
Water Vapourisation		.853				

(1) - Experimental Value

(2) - Higbie-Danckwerts Rates (relative)

(3) - Sherwood-Goodgame Formula

K_Ga - lb.mol./ft^3/hr./atm.

NOMENCLATURE for SECTION I

C = Average molal density of liquid, lb.mol./ft^3.

C_g = Concentration of solute in gas stream, % v/v.

c_e = Concentration of solute in liquid stream corresponding to equilibrium with gas, lb.mol./ft^3.

c_l = Concentration of solute in main body of the liquid, lb.mol./ft^3.

D_L = Liquid diffusivity, ft^2/hour.

D_V = Gas diffusivity, ft^2/hour.

G = Gas flow rate, ft^3/hour.

G_m = Molal mass velocity of gas, lb.mol./ft^2./hour.

H = Henry's Law constant, p_e/c_e.

k_Ga = Gas film coefficient on a volume basis, lb.mol./ft^3/hour/atm.

K_Ga = Overall gas film coefficient on a volume basis, lb.mol./ft^3/hour/atm.

k_La = Liquid film coefficient on a volume basis, lb.mol./ft^3.hour.unit conctn.

K_La = Overall liquid film coefficient on a volume basis, lb.mol./ft^2.hour.unit conctn.

L = Liquor rate, lbs./hour.

L_m = Liquor rate, lb.mol./hour.

m = H.C./P.

N_a = Absorption rate, lb.mol./ft^3/hour.

N_G = Number of individual gas film transfer units.

N_L = Number of individual liquid film transfer units.

N_{OG} = Number of overall gas film transfer units.

N_{OL} = Number of overall liquid film transfer units.

N_R = Rotor speed, r.p.m.

p_e/

p_e = Pressure of solute in equilibrium with concentration in main body of liquid, atm.

P = Total pressure on system, atm.

V = Volume of absorption apparatus, ft^3.

VTU_G = Volume of an individual gas film transfer unit, ft^3.

VTU_L = Volume of an individual liquid film transfer unit, ft^3.

VTU_{OG} = Volume of an overall gas film transfer unit, ft^3.

VTU_{OL} = Volume of an overal liquid film transfer unit, ft^3.

x_e = Mole fraction of solute in liquid at equilibrium with bulk of gas.

x_1 = Mole fraction of solute in liquid stream.

x_1 = Mole fraction of solute in inlet liquid stream.

x_2 = Mole fraction of solute in outlet liquid stream.

y = Mole fraction of solute in gas stream.

y_e = Mole fraction of solute in gas at equilibrium with bulk of liquid.

SECTION II

INTRODUCTION

In Section I of this work it was shown that absorption characteristics, in most of the systems considered, were masked by almost complete removal of the solute gas phase. Thus it seemed logical that construction of a smaller absorber with fewer rings would eradicate this difficulty in exact measurement.

The actual spray pattern formed in these rotary absorbers has not been studied visually because the units have been constructed in metal.[64,65,67]. It was therefore proposed to construct the essential parts of the new absorber in perspex. (See Fig. 16).

The absorption and desorption processes of ammonia and carbon dioxide with water as a liquid phase were studied in the new unit. Due to the restrictions imposed by gas entrance design in the multi-ring washer, large volumes could not be handled and counter-current working was considered impracticable. With the two ring absorber both of those failings could be remedied. It was not expected that counter-current working would

make/

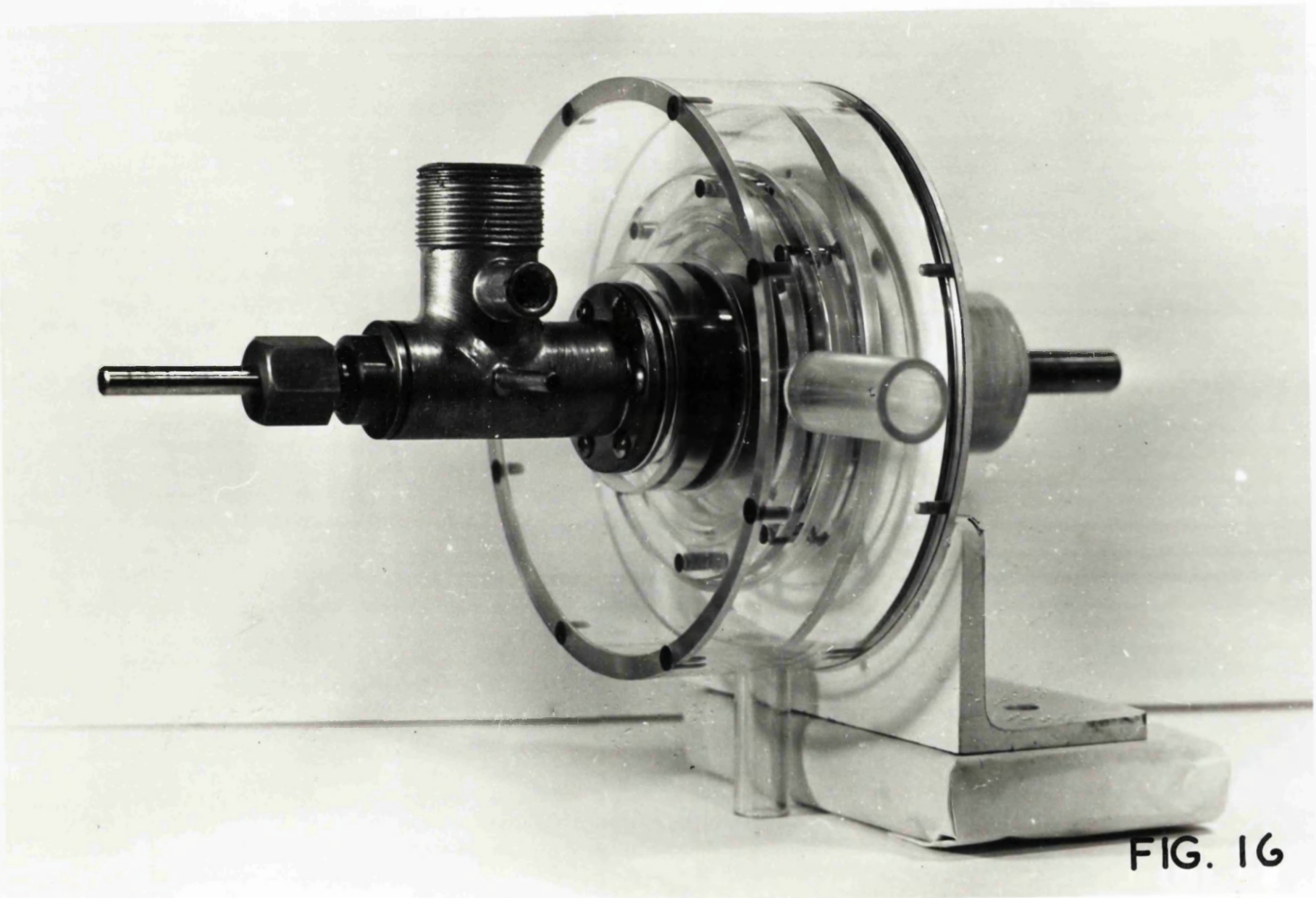
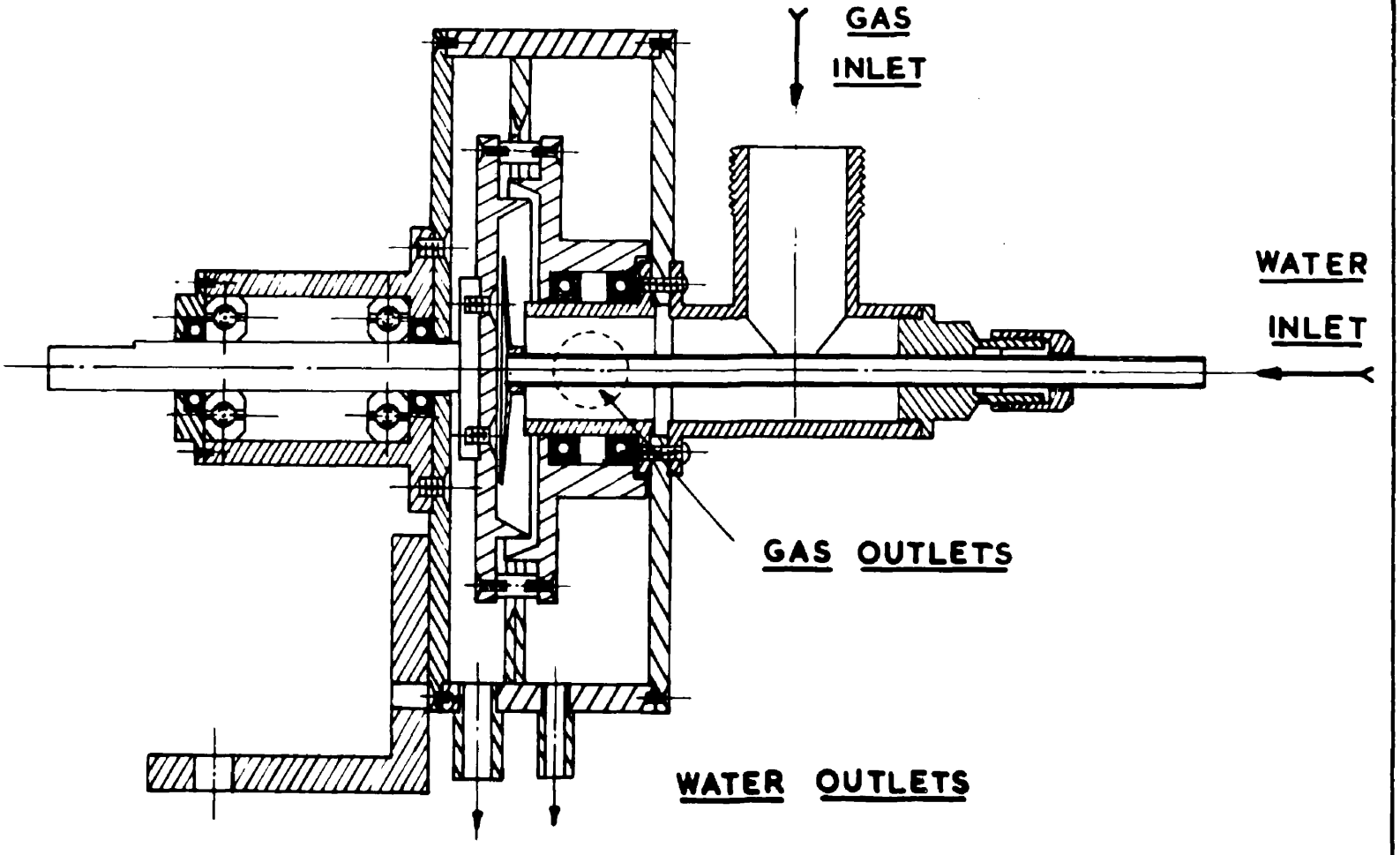


FIG. 16



DETAILS OF TWO-RING ABSORBER

FIG. 17

make much difference in mass transfer over any one stage as the gas, in considerably greater volumes than the liquid, was always travelling through the spray curtains in the earlier co-current tests. On the other hand, however, the centrifugal effect of the rotor would act against the gas flow, and the pressure drop would be more marked.

PLANT DESCRIPTION

(a) Absorber Details

A detailed drawing of the absorber is shown in Fig. 17. The assembly is erected for horizontal rotation of the drive shaft thus allowing the absorber plates to rotate in the vertical plane common with the multi-ring absorber. Constructed of perspex, each plate has one ring of triangular cross section attached to it - the ring on the first plate is 4" in diameter and on the second 4½" in diameter. The plates are held ½" apart by eight stainless steel distance pieces and the two rings intermesh leaving 1/8" clearance between the tip of the rings and the adjacent plate. The plate assembly is bolted to the flanged drive shaft which passes through two ball races/

races acting as the bearing support. The plate which is not connected directly to the shaft has a 2" I.D. perspex cylinder attached co-axially to it, in which two rubber seals bear against the $1\frac{1}{2}$" O.D. stainless steel gas inlet tube in the absorber. This gas inlet tube is $1\frac{1}{4}$" I.D. and leads the gas straight in to the absorber ring. Liquor enters the absorber through a $\frac{5}{16}$ ths O.D. x $\frac{1}{4}$" I.D. stainless steel tube inserted co-axially through the gas inlet tube. The end of this liquor tube has a $2\frac{3}{4}$" diameter plate flanged on to it allowing the liquor to spread over the face of the first plate without premature disruption from the gas flow. The absorber plate assembly is housed in a cylindrical perspex case with a steel back to which the ball race housing is attached. Separation of the phases is effected by means of an annular baffle plate mounted in the cylindrical case at the optimum position for splitting liquid and gas flow. The liquor is thrown almost completely to the rear of the casing, from which it drains via a $\frac{1}{2}$" I.D. pipe (later two) - the gas passing to the front compartment in the casing and leaving by two $\frac{3}{4}$" I.D. pipes. There is a supplementary $\frac{1}{4}$" I.D. liquor drain pipe/

pipe in this front compartment for any liquor carried out in the gas stream or flooding in from the rear compartment.

(b) Plant Details

The absorber is driven by a 1/4 H.P. D.C. motor reostatically controlled for speed variation between 100 and 3000 r.p.m. The liquor is delivered to the absorber by a centrifugal pump with a controlable by-pass. The flow rate is indicated on a "Rotameter" gauge. Air for the inert gas stream is supplied by an electrically driven vane blower capable of delivering 4000 ft^3/hour. An orifice plate differential monometer is calibrated to give the flow rate of air. The solute gas (in the case of the absorption tests) is supplied from cylinders of anhydrous ammonia or carbon dioxide and flow rates are indicated on an orifice plate differential monometer. a/

EXPERIMENTAL

When working with ammonia, analysis in the liquid phase was made by normal titration with sulphuric acid and methyl red as indicator. For carbon dioxide absorption and desorption tests the method of analysis for/

for carbon dioxide in water given by McKinney and Amorosi[66] was used. Gas sampling was carried out in the usual way. In all the absorption tests mass balances were established before a test could be accepted. A special device for obtaining a sample of the water as it was flung from the plates was constructed and results from this sampling point showed no great difference from those obtained with samples from the drain pipe from the absorber case. In desorption tests, using ammonia, the liquid used was .88 S.G. ammonia liquor diluted to a normality of 1 - 2. In the case of carbon dioxide, solid dry-ice was added to a tank full of water and allowed to saturate it.

The first range of tests determined the pressure drop in counter-current as compared with co-current working and Fig. 18 shows that the expected results have been obtained. The pressure drop for counter-current flow is anything up to four times the value for co-current working under comparable conditions.

In the next series of tests the rate of absorption of carbon dioxide was measured. The effects of varying (a) gas rate (b) water rate and (c) rotor speed in co-current and counter-current flow are set out in Figs. 19/

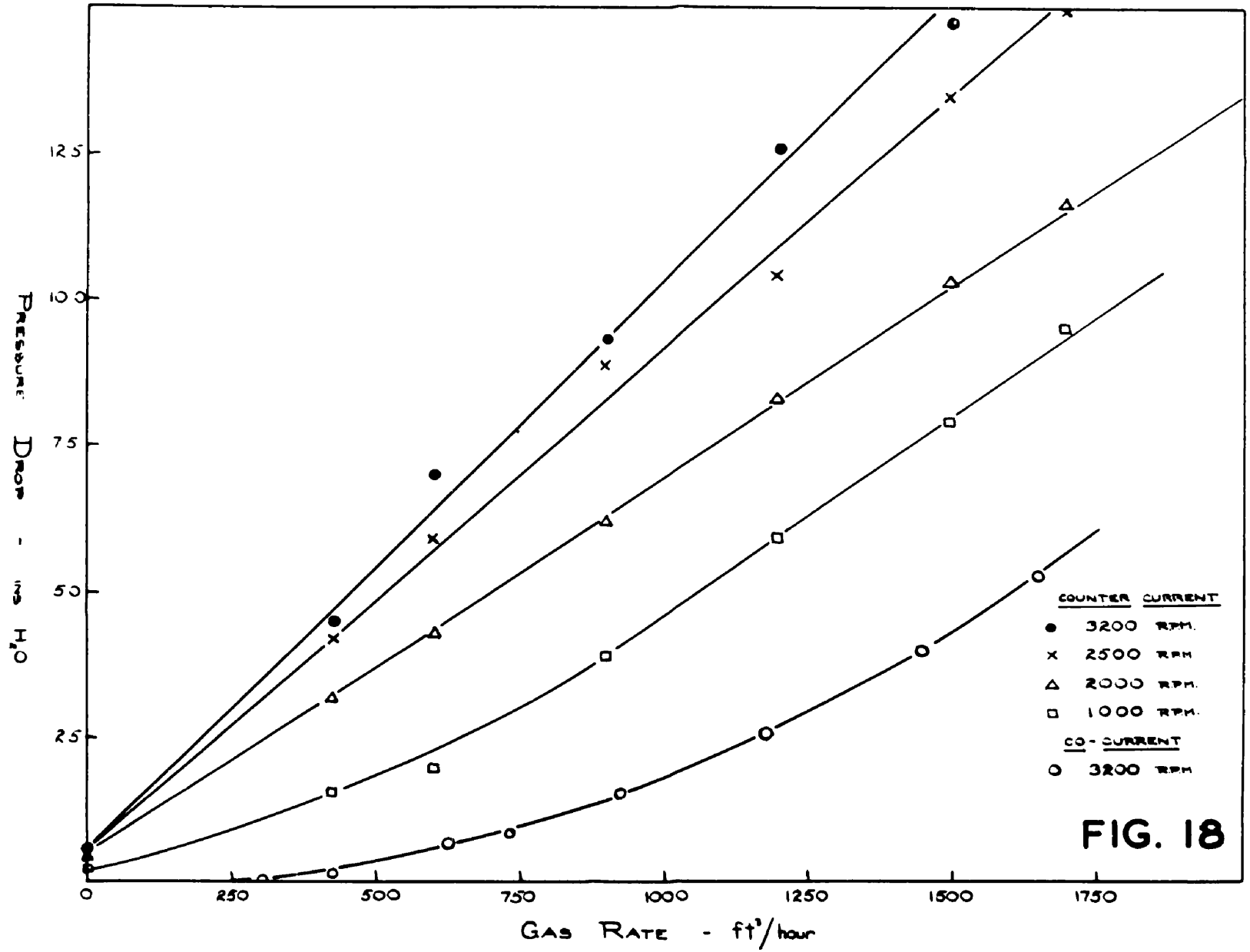

Pressure Drop - ins H2O
125
100
75
50
25
0
250
500
750
1000
1250
1500
1750
Gas Rate - ft³/hour
COUNTER CURRENT
3200 RPM.
2500 RPM
2000 RPM.
1000 RPM.
CO-CURRENT
3200 RPM

FIG. 18

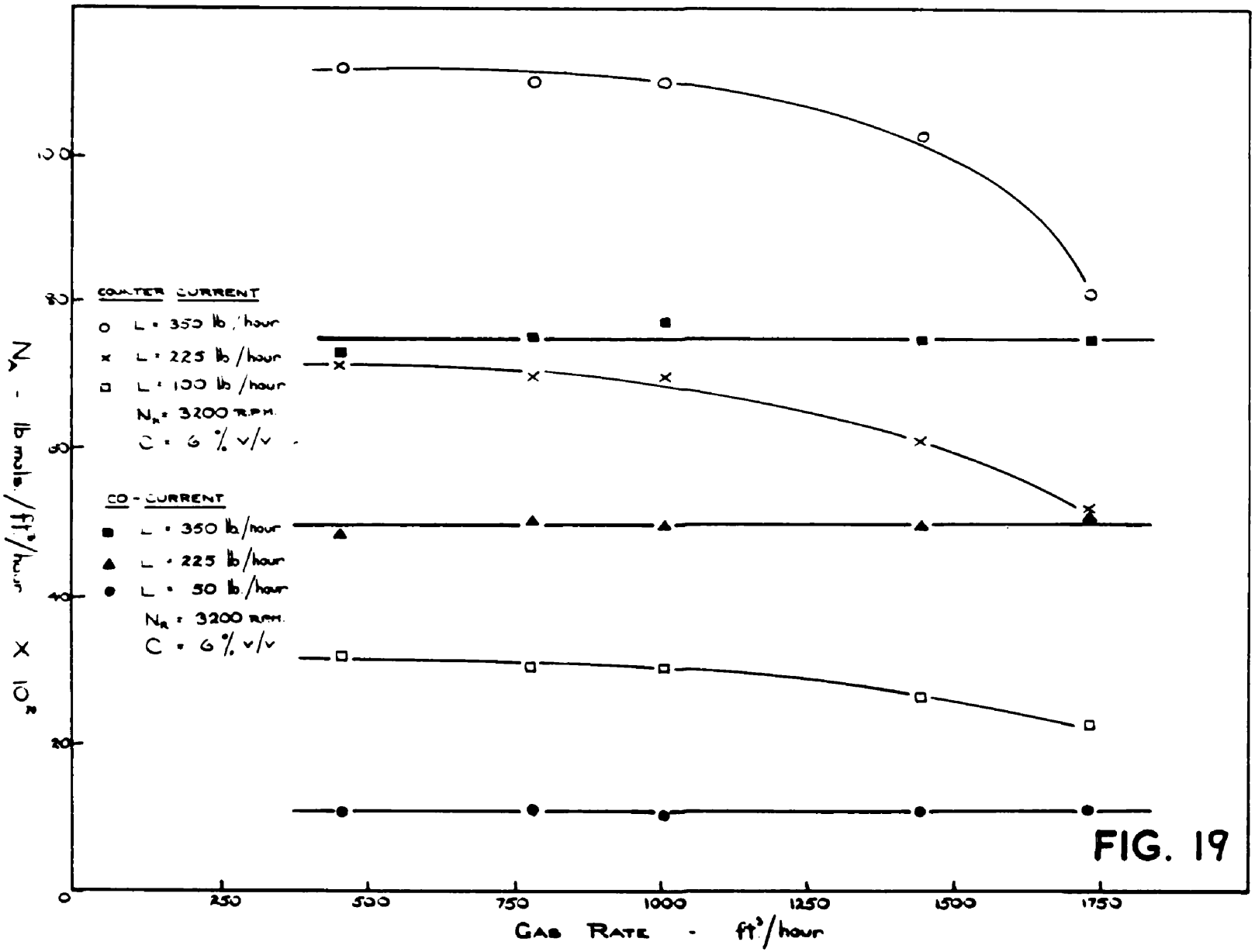

COUNTER CURRENT
L = 350 lb./hour
L = 225 lb/hour
L = 100 lb/hour
N_R = 3200 R.P.M.
C = 6 % v/v
CO-CURRENT
L = 350 lb/hour
L = 225 lb/hour
L = 50 lb/hour
N_R = 3200 R.P.M.
C = 6 % v/v
N_A - lb mole/ft²/hour X 10^2
0
20
40
60
80
100
250
500
750
1000
1250
1500
1750
Gas Rate - ft³/hour

FIG. 19

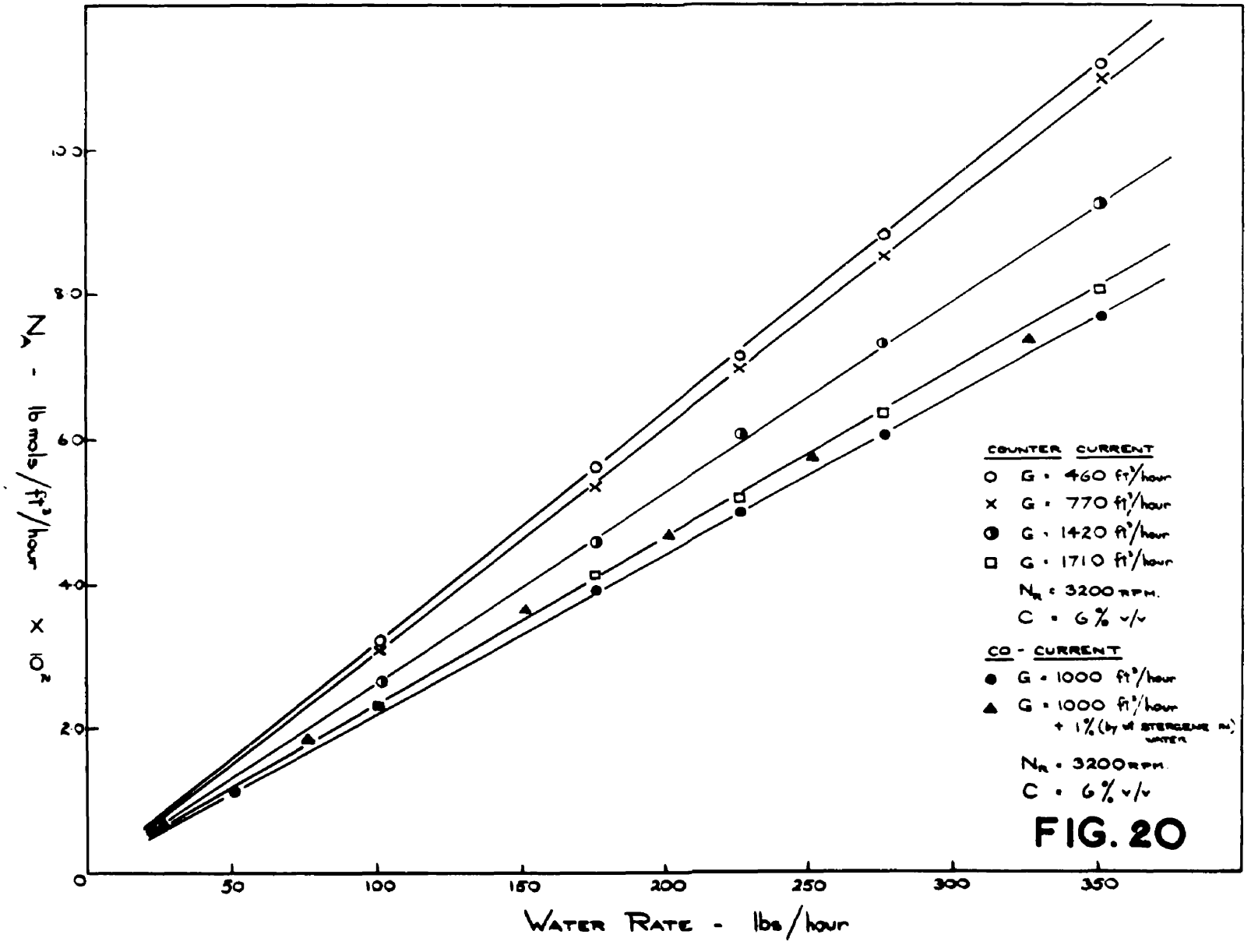

N_A - lb mols/ft²/hour X 10^2
0
2.0
4.0
6.0
8.0
10
50
100
150
200
250
300
350
WATER RATE - lbs/hour
COUNTER CURRENT
G = 460 ft³/hour
G = 770 ft³/hour
G = 1420 ft³/hour
G = 1710 ft³/hour
N_R = 3200 RPM.
C = 6% v/v
CO - CURRENT
G = 1000 ft³/hour
G = 1000 ft³/hour
+ 1% (by wt STERGENE IN) WATER
N_R = 3200 RPM.
C = 6% v/v

FIG. 20

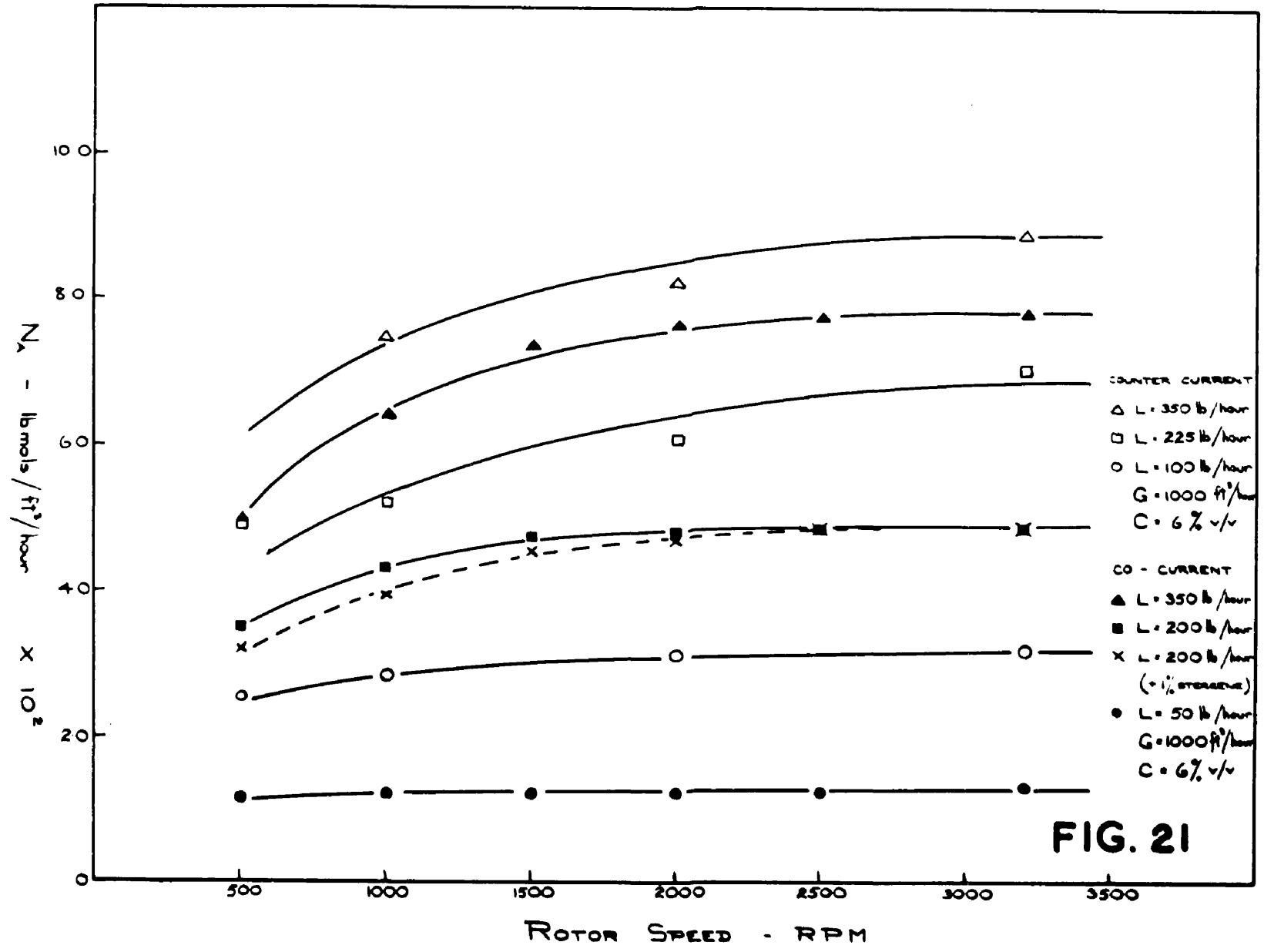

10 0
8 0
6 0
4 0
2 0
0
N_A - lb mols / ft³ / hour X 10²
500
1000
1500
2000
2500
3000
3500
Rotor Speed - RPM
COUNTER CURRENT
△ L = 350 lb/hour
□ L = 225 lb/hour
○ L = 100 lb/hour
G = 1000 ft³/hour
C = 6 % v/v
CO - CURRENT
▲ L = 350 lb/hour
■ L = 200 lb/hour
× L = 200 lb/hour
(+ 1% STEARENE)
● L = 50 lb/hour
G = 1000 ft³/hour
C = 6% v/v

FIG. 21

19, 20 and 21. As in earlier work the effect of gas rate is negligible in co-current working, while in counter-current flow the rate of absorption decreases as gas velocity increases. The comparative rates of absorption in the two methods of flow are slightly higher for counter-current working, with a falling off almost to equal values with high gas rates.

The rates of mass transfer vary directly with liquid rate, as in all the earlier work. Both in co-current and counter-current working the results show a direct linear relationship with perhaps a slight falling off at very high liquid rates. Traces of stergene made no difference to results.

Finally the effects of rotor speeds show a slow increase in N_a at first, followed by a virtually stationary valve as the speed goes up from 2000 to 3300 r.p.m.

In the next series of tests, ammonia was the solute gas, and in addition to varying liquid and gas rates with rotor speeds, a variety of surface active agents were added to the water before absorption. The effect of the first variable is shown in Fig. 22, when it will be seen that N_a is no longer a linear function of the liquid/

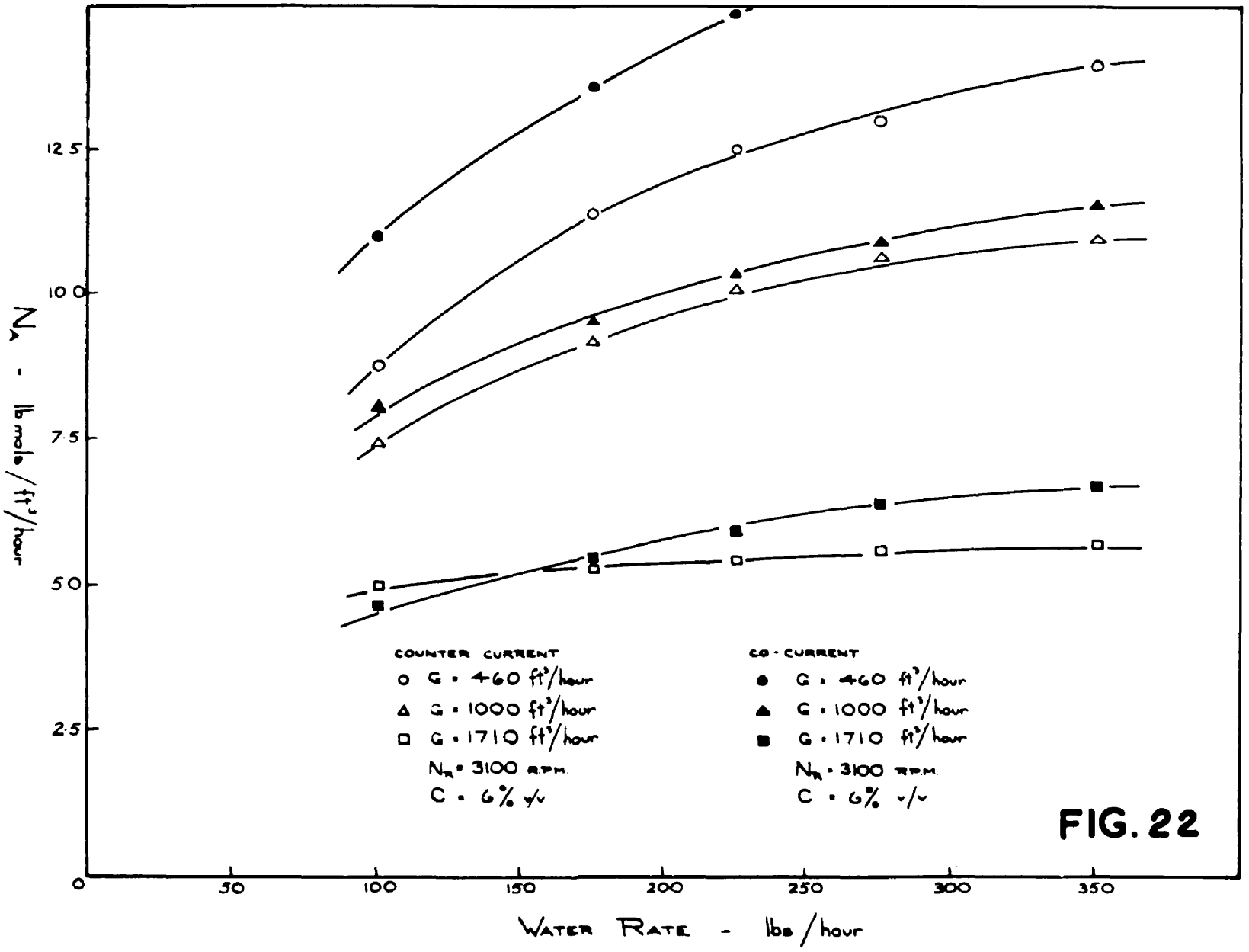

12.5
10.0
7.5
5.0
2.5
0
50
100
150
200
250
300
350
N_A - lb mols / ft³ / hour
WATER RATE - lbs / hour
COUNTER CURRENT
○ G = 460 ft³/hour
△ G = 1000 ft³/hour
□ G = 1710 ft³/hour
N_R = 3100 R.P.M.
C = 6% v/v
CO-CURRENT
● G = 460 ft³/hour
▲ G = 1000 ft³/hour
■ G = 1710 ft³/hour
N_R = 3100 R.P.M.
C = 6% v/v

FIG. 22

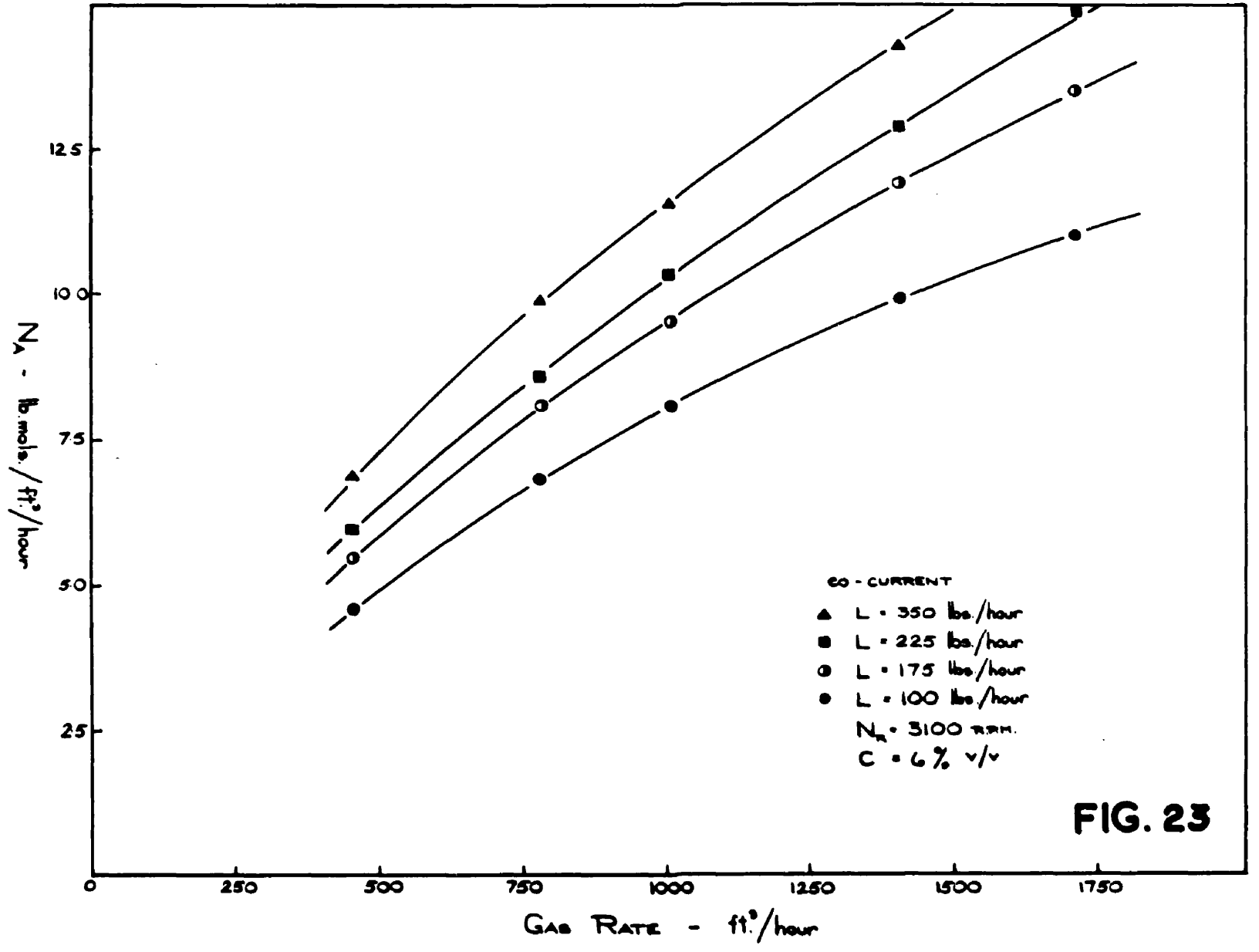

12.5
10.0
7.5
5.0
2.5
N_A - lb.mole./ft.²/hour
0
250
500
750
1000
1250
1500
1750
Gas Rate - ft.³/hour
CO - CURRENT
L = 350 lbs./hour
L = 225 lbs./hour
L = 175 lbs./hour
L = 100 lbs./hour
N_{Re} = 3100 APPX.
C = 6 % v/v

FIG. 23

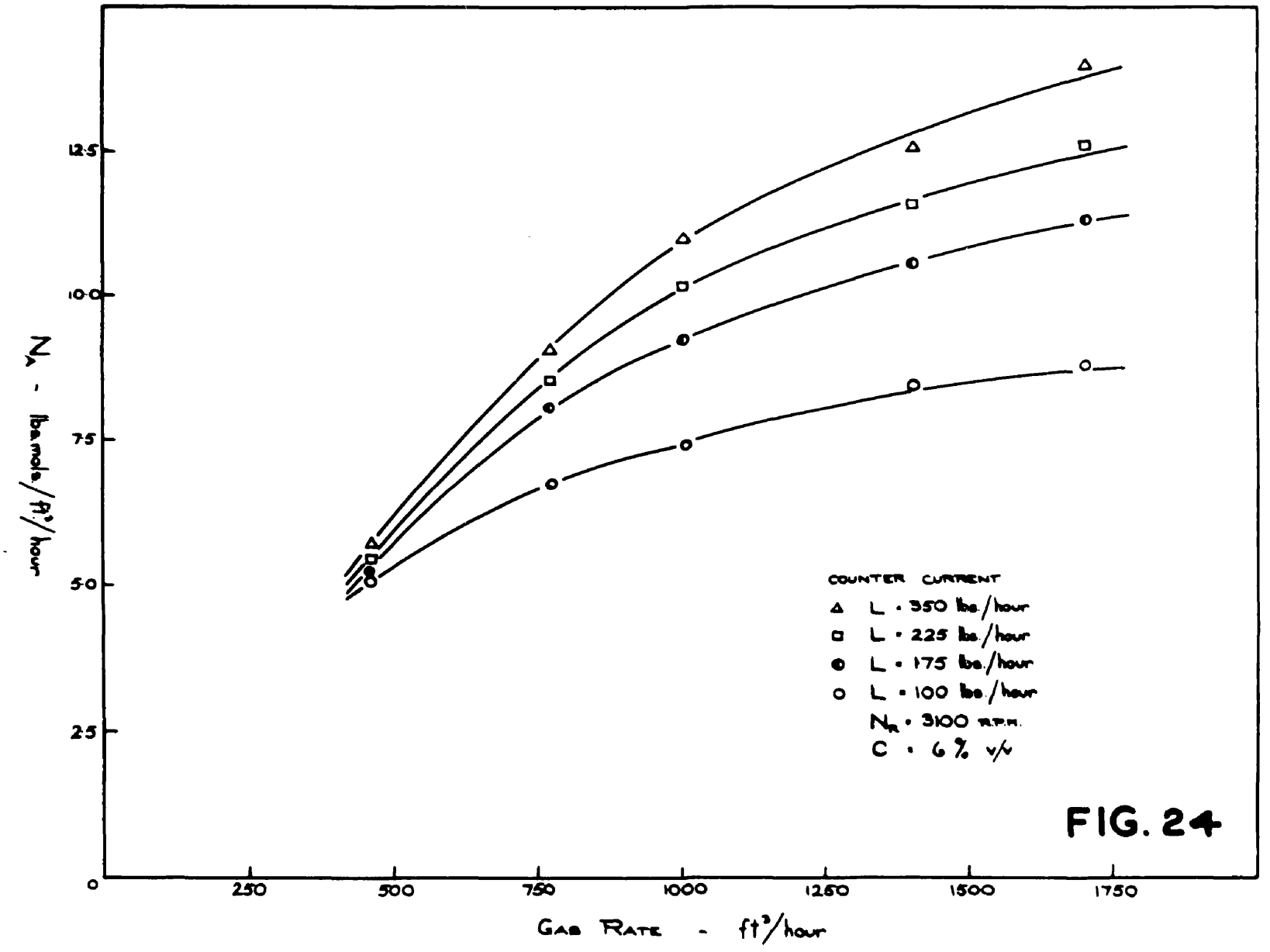

12.5
10.0
7.5
5.0
2.5
0
N_A - lbs.mols/ft³/hour
250
500
750
1000
1250
1500
1750
Gas Rate - ft³/hour
COUNTER CURRENT
△ L = 350 lbs./hour
□ L = 225 lbs./hour
● L = 175 lbs./hour
○ L = 100 lbs./hour
N_R = 3100 R.P.M.
C = 6 % v/v

FIG. 24

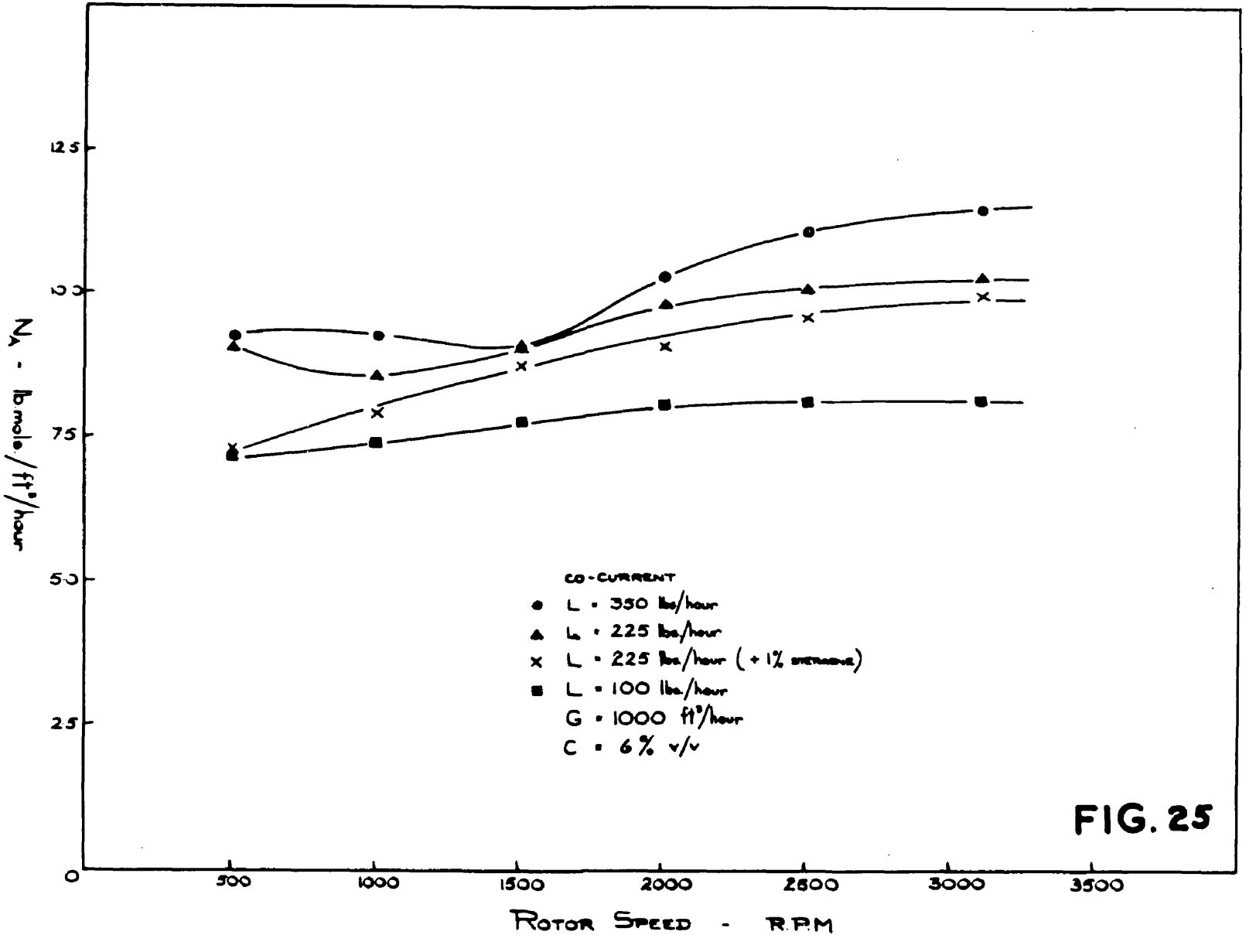

125
100
75
50
25
0
N_A - lb mole/ft³/hour
500
1000
1500
2000
2500
3000
3500
Rotor Speed - R.P.M
CO-CURRENT
L = 350 lbs/hour
L = 225 lbs/hour
L = 225 lbs/hour (+1% ETHANOL)
L = 100 lbs/hour
G = 1000 ft³/hour
C = 6% v/v

FIG. 25

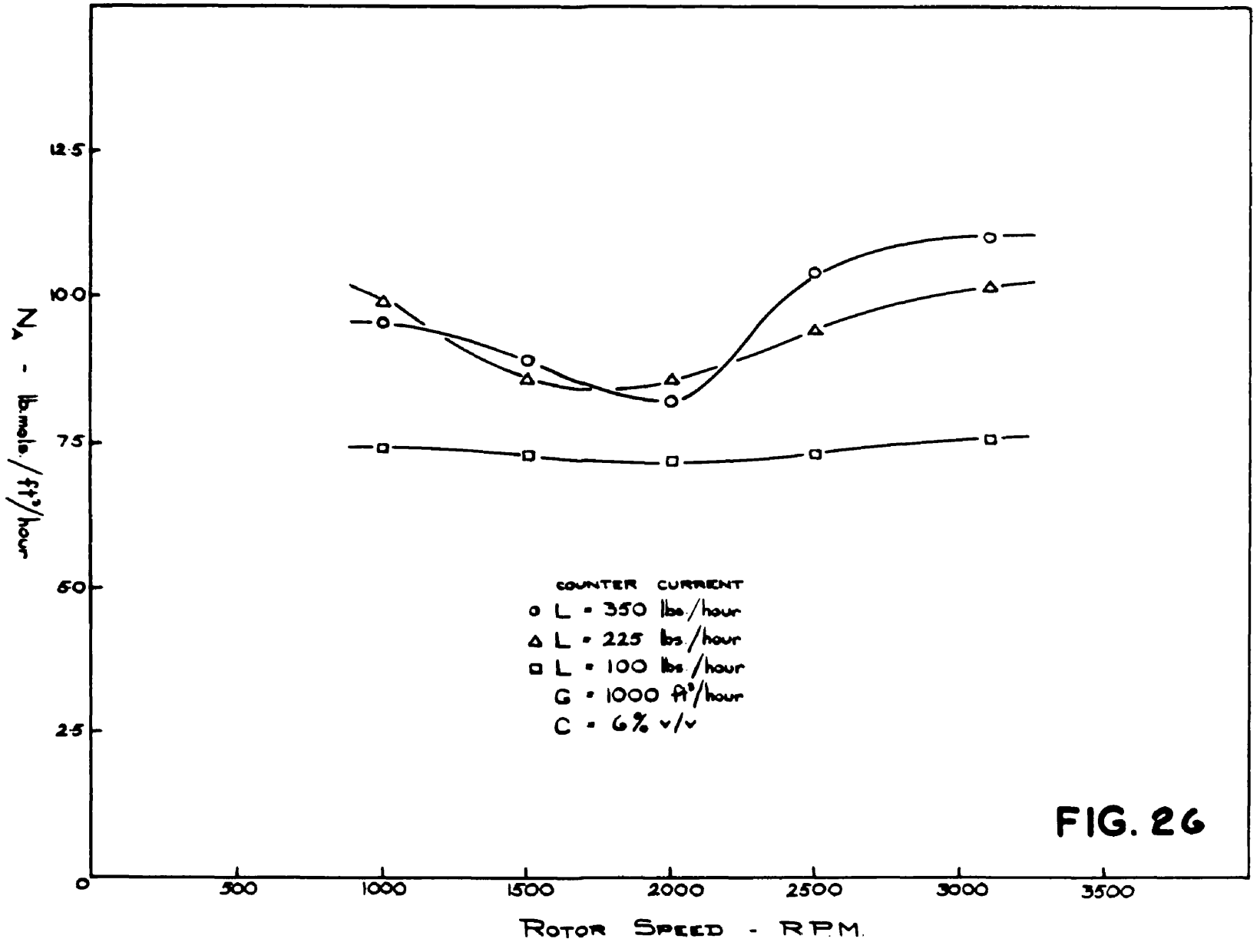

12.5
10.0
7.5
5.0
2.5
0
N_A - lb.mole/ft³/hour
500
1000
1500
2000
2500
3000
3500
Rotor Speed - RPM.
COUNTER CURRENT
o L = 350 lbs./hour
Δ L = 225 lbs./hour
□ L = 100 lbs./hour
G = 1000 ft³/hour
C = 6% v/v

FIG. 26

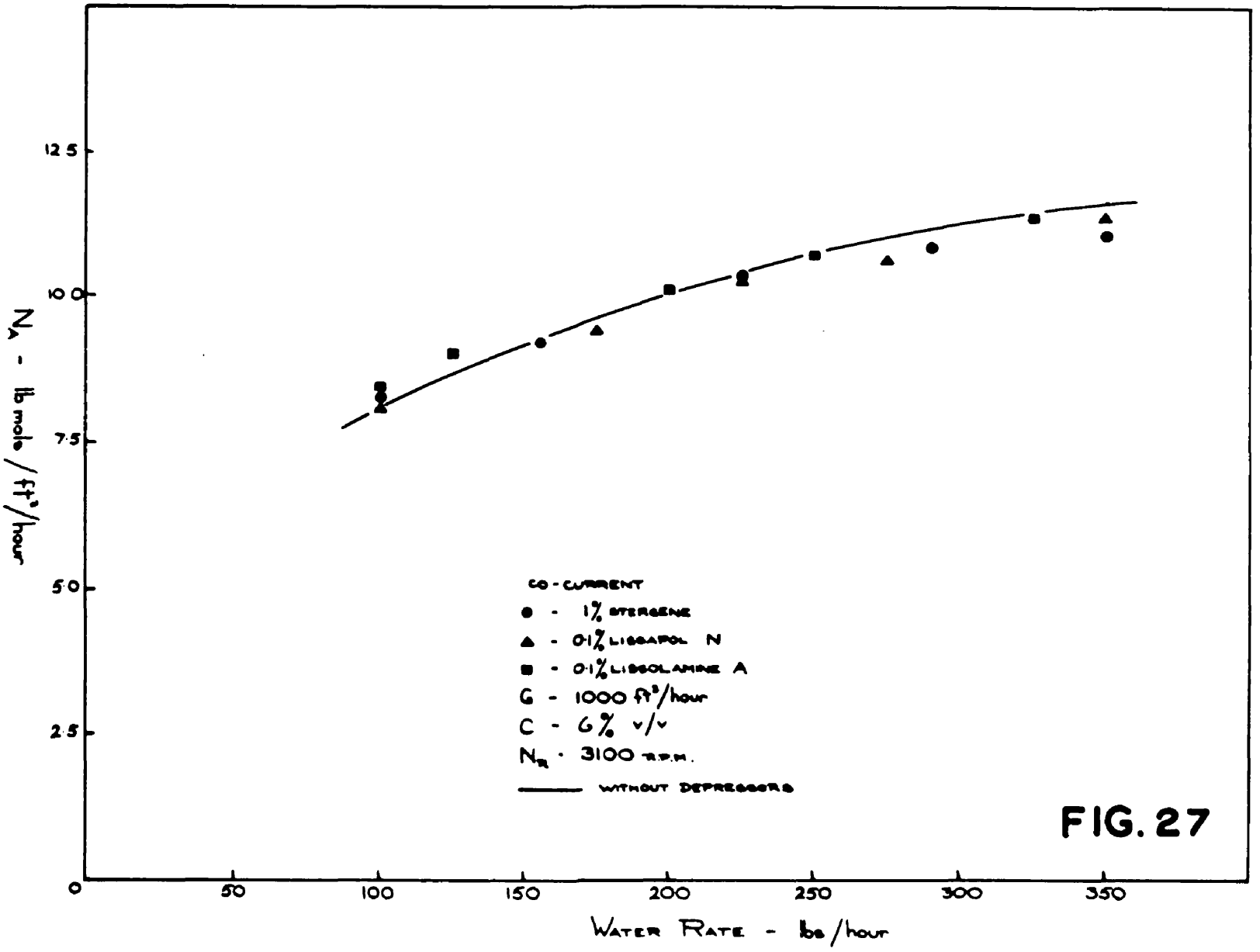

12.5
10.0
7.5
5.0
2.5
0
50
100
150
200
250
300
350
N_A - lb mole / ft³/hour
Water Rate - lbs/hour
CO-CURRENT
● - 1% SYNTHRENE
▲ - 0·1% LISSAPOL N
■ - 0·1% LISSOLAMINE A
G - 1000 ft³/hour
C - 6% v/v
N_R - 3100 R.P.M.
——— WITHOUT DEPRESSORS

FIG. 27

liquid rate but only increases relatively slowly, either in co- or counter-current flow. In co-current flow the effect of gas rate was very similar to that of the liquid (Fig. 23) but in counter-current flow (Fig. 24) the mass transfer was actually constant at high gas rates (i.e. the value of N_a was independent of the gas rate). Rotor speed effects were uneven, and there seems to be some evidence of a change in drop formation around the middle range of speed (Fig. 25).

Change of this kind, without a corresponding alteration when carbon dioxide is being absorbed, suggested that the ammonia was giving a sharp alteration in surface tension on absorption. A test using detergent solution (0.1% Stergene) certainly seemed to give more regular form to the Rotor Speed v. N_a curve as will be seen from Fig. 26. On the other hand, a wide range of surface active agents made very little difference to total absorption (Fig. 27) a point that will be discussed later.

Experiments were now carried out on the reverse case - the desorption of carbon dioxide and ammonia from liquid solutions. In the first series a saturated solution of carbon dioxide was pumped through the washer, with/

with air flowing co-current. The carbon dioxide in solution was estimated before and after test. Again the normal variables of liquid flow, gas flow and rotor speed were measured against $K_L a$, (as inlet concentration varied considerably), with the results set out in Figs. 28, 29 and 30.

From Fig. 28, it will be seen that the gas rate has no effect whatever on the mass transfer coefficient in desorption. As usual, the liquid rate (Fig. 29) largely determines the rate of mass transfer, but there is a definite falling off from a linear relationship at high liquid rates. This suggests a flooding condition may be reached - a possible limiting factor that has been avoided in the large rotor by the powerful pumping effect of the outer rings. This centrifugal pumping action has been supposed (Section I) to cut down the contact time and thus mask the effect of rotor speed increase in the more effective dispersion of liquid. A single ring system would perhaps show this more effective dispersion, and in fact this has been the case (Fig. 30).

Now the desorption of carbon dioxide, with such small concentrations of the solute gas in the gas phase will almost certainly be controlled by the liquid phase conditions/

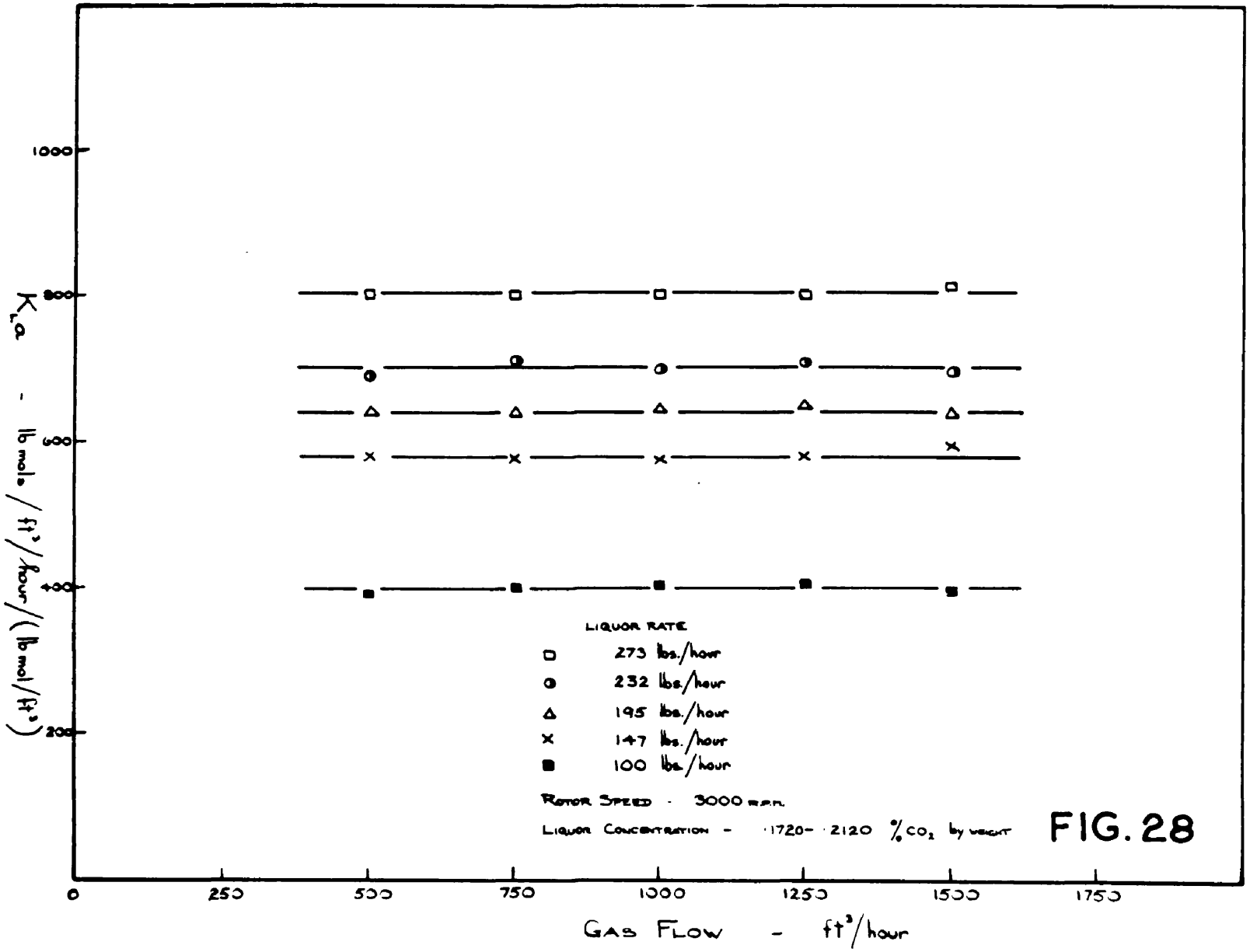

1000
800
600
400
200
$K_L a$ - lb mole / ft³ / hour / (lb mol/ft³)
0
250
500
750
1000
1250
1500
1750
Gas Flow - ft³/hour
LIQUOR RATE
273 lbs./hour
232 lbs./hour
195 lbs./hour
147 lbs./hour
100 lbs./hour
Rotor Speed - 3000 r.p.m.
Liquor Concentration - 1720 - 2120 % CO_2 by weight

FIG. 28

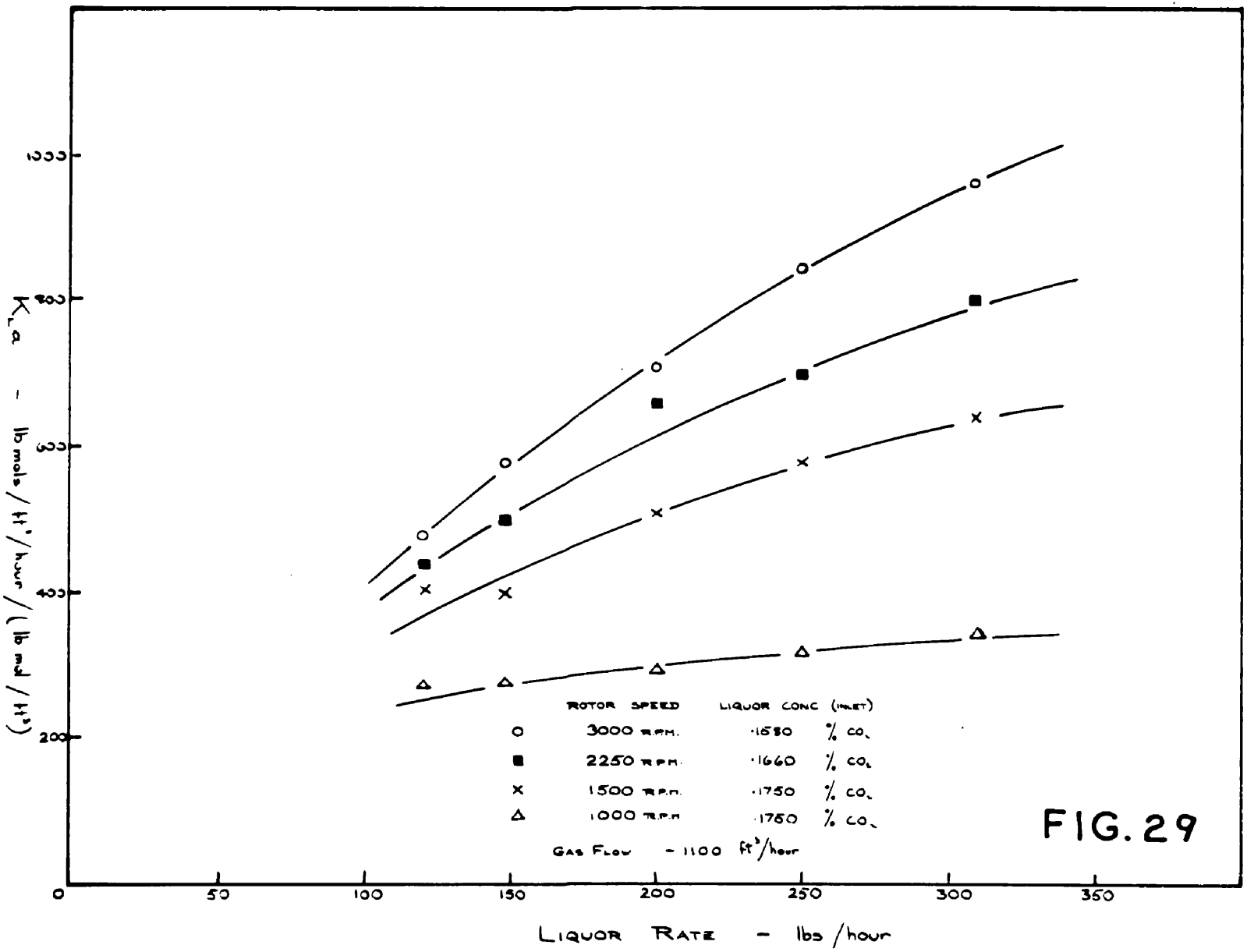

K_La - lb mols / ft³ hour / (lb mol / ft³)
200
300
400
500
0
50
100
150
200
250
300
350
Liquor Rate - lbs / hour
Rotor Speed
Liquor Conc (inlet)
3000 R.P.M. .1580 % CO_2
2250 R.P.M. .1660 % CO_2
1500 R.P.M. .1750 % CO_2
1000 R.P.M. .1760 % CO_2
Gas Flow - 1100 ft³/hour

FIG. 29

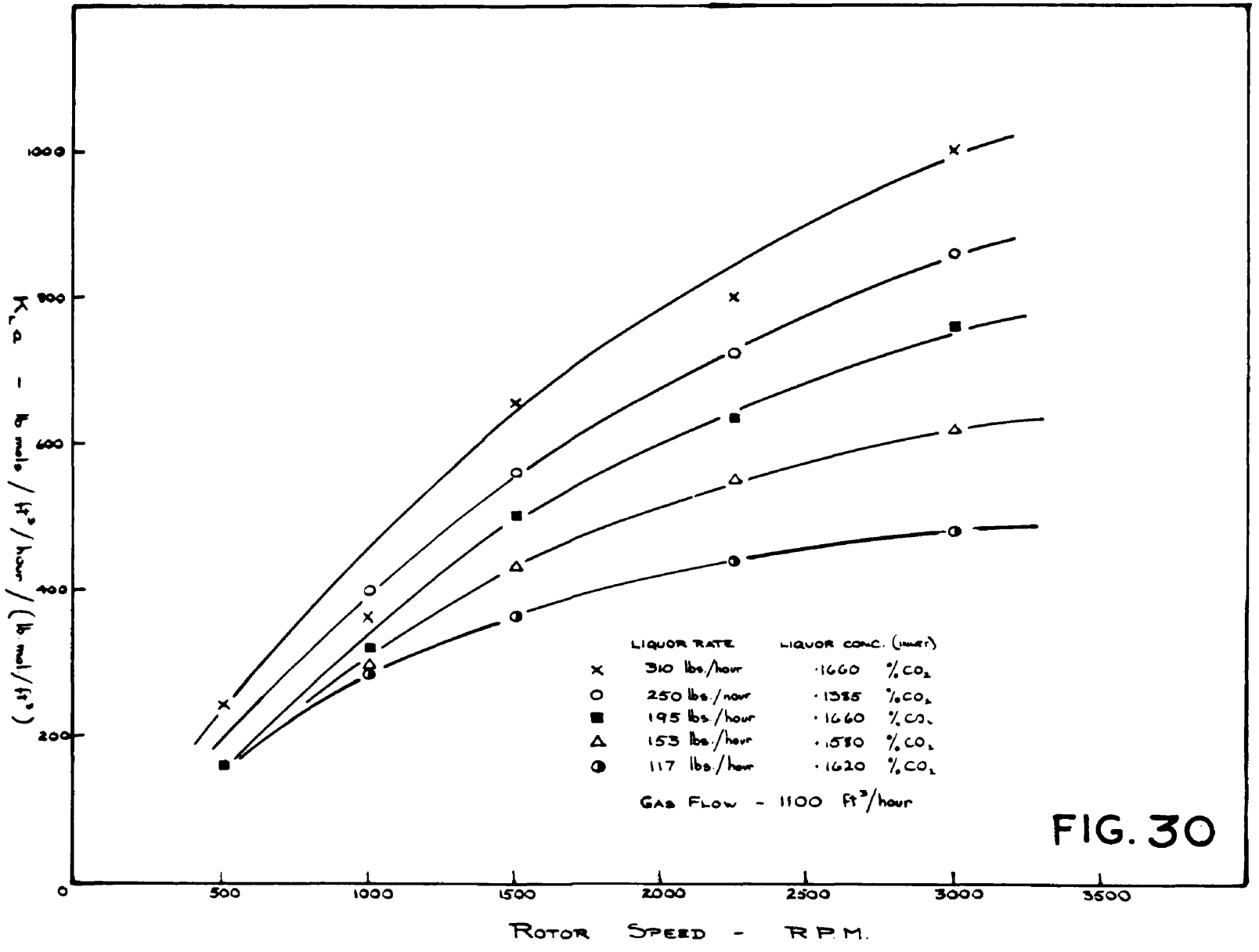

1000
800
600
400
200
0
500
1000
1500
2000
2500
3000
3500
$K_L a$ - lb mols / hour / ft³ / (lb mols / ft³)
Rotor Speed - R.P.M.
LIQUOR RATE
LIQUOR CONC. (INLET)
× 310 lbs./hour ·1660 % CO_2
○ 250 lbs./hour ·1355 % CO_2
■ 195 lbs./hour ·1660 % CO_2
△ 153 lbs./hour ·1580 % CO_2
◑ 117 lbs./hour ·1620 % CO_2
Gas Flow - 1100 ft³/hour

FIG. 30

conditions. The opposite effect will be present, at any rate in part, when ammonia is passing from water to gas. Even in the one ring unit, however, the old problem is encountered (see Section I) in that equilibrium is very nearly attained in some experiments. As a result, the values for the mass transfer coefficients are in some doubt. The results are represented in Figs. 31, 32 and 33.

In the first place (Fig. 31) the effect of gas rate is uncertain, and may well be markedly influenced by near approach to equilibrium at low liquor and gas flows. The effect of increasing liquor rates is still more doubtful, but it does appear clear that the liquid rate is no longer the really determining variable (Fig. 32). Finally the speed of the rotor has no consistent effect, and seems in fact to suggest a vague maximum for any one liquid rate for which the dispersion is at its best.

Spray Formation

The washer was made of perspex, and it was therefore possible to examine the liquid dispersion visually, using stroboscopic lighting where necessary. When

flow/

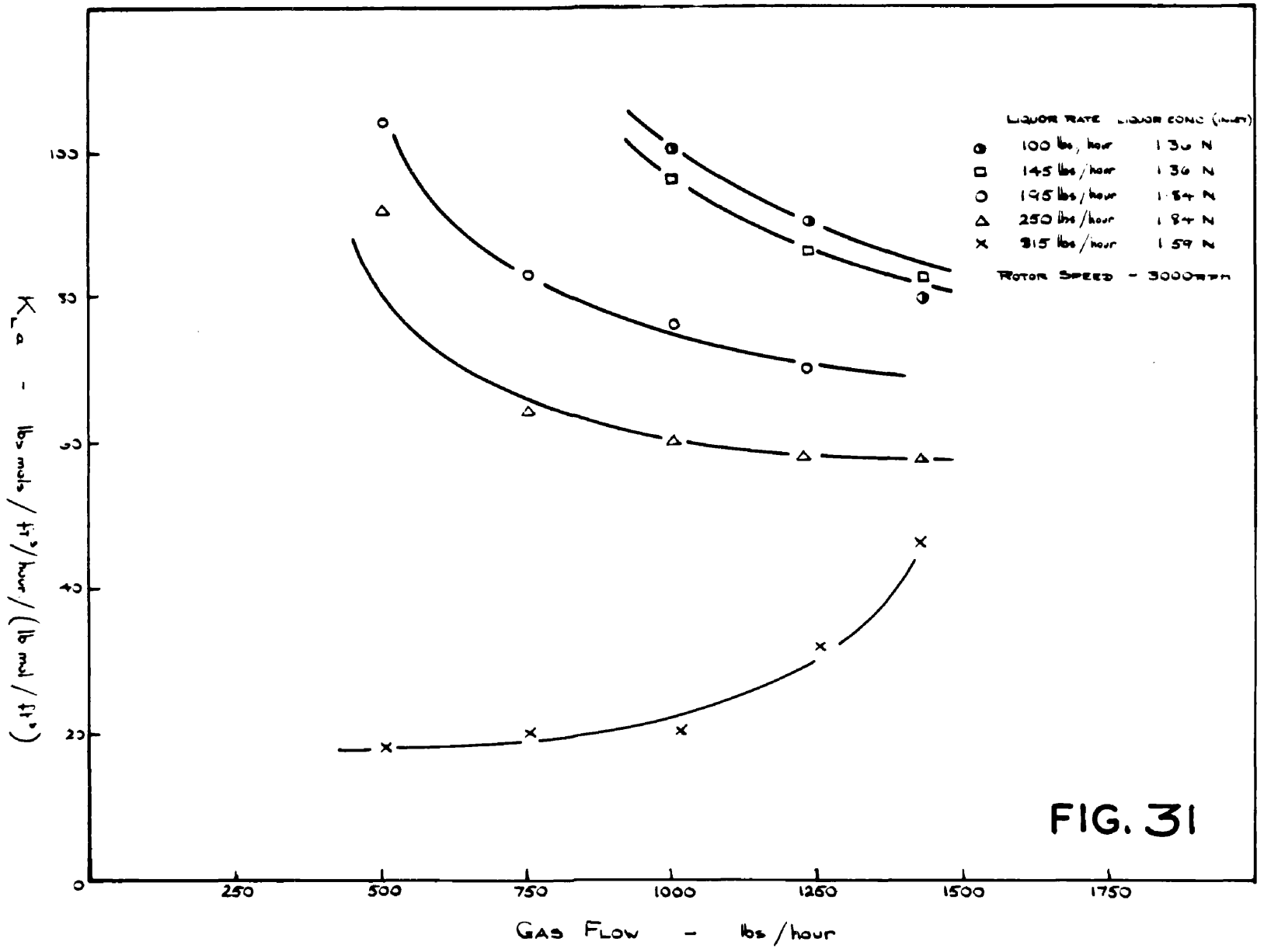

LIQUOR RATE
LIQUOR CONC (INLET)
100 lbs/hour 1.36 N
145 lbs/hour 1.36 N
195 lbs/hour 1.84 N
250 lbs/hour 1.84 N
315 lbs/hour 1.59 N
ROTOR SPEED - 3000 RPM
$K_L a$ - lbs mols / ft³ / hour / (lb mol / ft³)
0
20
40
60
80
100
250
500
750
1000
1250
1500
1750
GAS FLOW - lbs / hour

FIG. 31

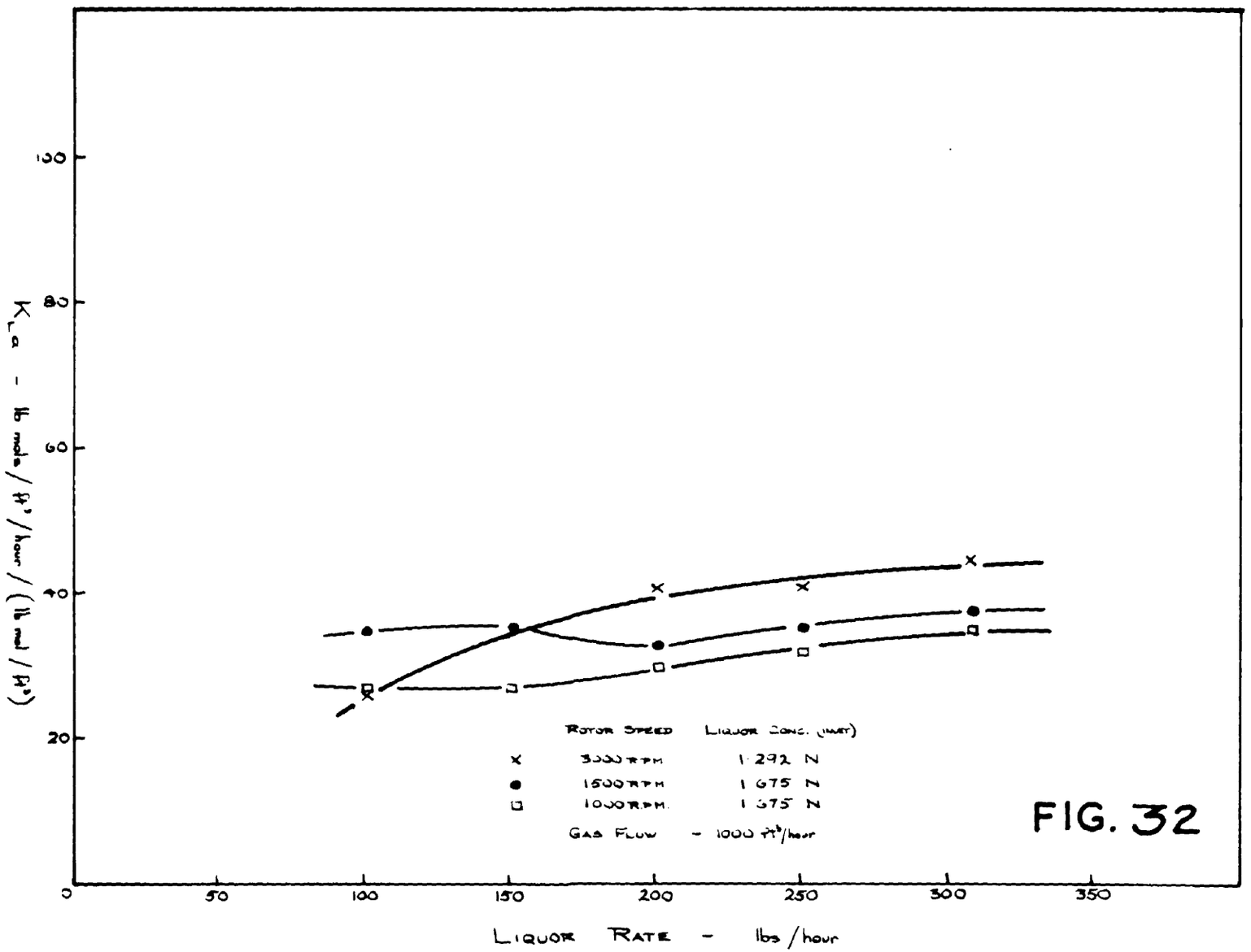

K_La - lb mols / ft³ / hour / (lb mol / ft³)
0
20
40
60
80
100
50
100
150
200
250
300
350
Liquor Rate - lbs / hour
Rotor Speed
Liquor Conc. (wt%)
3000 RPM
1.292 N
1500 RPM
1.675 N
1000 RPM
1.675 N
Gas Flow - 1000 ft³/hour

FIG. 32

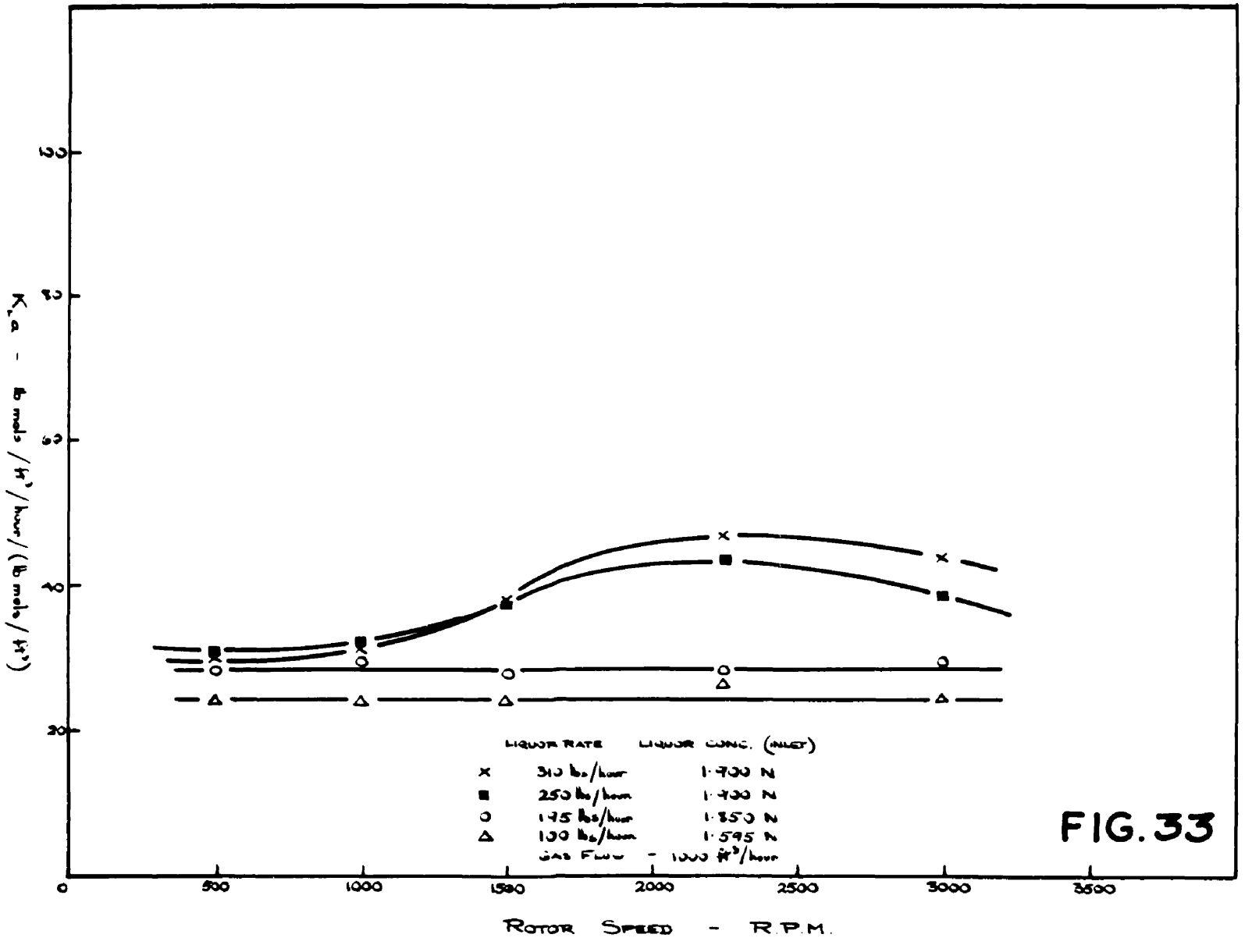

$K_L a$ - lb mols / ft³ / hour / (lb mols / ft³)
50
40
30
0
500
1000
1500
2000
2500
3000
3500
Rotor Speed - R.P.M.
LIQUOR RATE
LIQUOR CONC. (INLET)
× 310 lbs/hour 1·930 N
■ 250 lbs/hour 1·930 N
○ 195 lbs/hour 1·350 N
△ 130 lbs/hour 1·595 N
Gas Flow - 1000 ft³/hour

FIG. 33

flow was co-current, the form of the liquid spray seemed to be principally determined by rotor speed. A series of fine jets of fluid formed on the edge of the inner ring, and the higher the speed the finer the jets. These jets impinged on the outer ring and reformed again at the tip. Generally the jet broke up into droplets before the space between the rings was passed. As the rotor speed diminished, the jets were less numerous and coarser; finally at about 500 r.p.m., the liquid left the rim as a film, which broke into drops and, in this form, impinged on the outer ring. The films forming at the rim grew wider as the rotor speed slackened, or alternatively as the liquid feed rate increased. They were, however, broken by either gas stream or hydrodynamic forces before the next ring was reached.

With counter-current flow, at rotor speeds above 1500 r.p.m., the appearance of the spray was very similar for all gas rates up to about 1000 ft^3/hour, but then the gas started to interfere quite notably with liquid flow. High gas rates appeared to cause coalescence with formation of larger drops, but this optical effect might only have been due to the carrying over of/

of the finer droplets.

As far as could be seen, no surface active agent caused any notable modification in the types of liquid spray formed. This rather surprising result is, of course, borne out by the trifling effects of surface active additions on absorption rates.

Discussion of results obtained in single ring washer

It is immediately clear that counter-current flow of gas and liquid does not increase contacting efficiency. In fact, considering the greatly increased pressure drop, it may be stated that washers of this kind work better with gas and liquid flowing in the same direction. It follows that the real contacting mechanism is the movement of liquid droplets through the gas phase at high speed in the spray curtain area.

In these circumstances, the rotor spins to give a definite surface of liquid per unit volume of liquid. This surface is rapidly saturated by carbon dioxide and the time of contact is so short that diffusion into the droplet interior does not occur. Then the amount of carbon dioxide absorbed and hence the value of N_a or $K_L a$ is directly proportional to the amount of water used - a mechanism that appears to be well established

both/

both here and in previous reports.[3] Change to counter-current working slightly improves surface formation at low gas rates, but the effect is negligible at higher gas flows.

In view of the improved dispersion given by higher rotor speeds, it is a trifle surprising that corresponding increase in absorption can be detected. In desorption, however, there is a definite increase of mass transfer with rotor speed. The centrifugal effect in the single ring rotor is relatively small, and decreases in contact time cannot offset smaller droplets - as was suggested with the multi-ring washer (Section I). Perhaps some surface tension alteration has occured - a point which will be returned to later.

When ammonia is being absorbed, the surface of the liquid is never fully saturated and the gas film, which normally shows much more rapid diffusion rates than the liquid film, may become important. A slow increase in N_a for NH_3 absorption with both liquid and gas rates, which has been noted, illustrates this fact. Rotor speed effects are uneven, and it may be that ammonia is having some effect on the drop formation through changes in surface tension. The desorption of ammonia, with relatively/

relatively small changes of concentration in the liquid surface film, should not show such dependence on liquid rates, and should be rather dependent on gas - liquid velocities. The relative movement between liquid drops and gas stream may be obscure and combine with rotor speed to give a confused set of results, and this is in fact the case of Figs. 31, 32 and 33.

NOMENCLATURE for SECTION II

$K_L a$ = Overall liquid side coefficient, lb.mols./ft^2/hour/(lb.mol./ft^3)

N_a = Absorption rate, lb.mols./ft^3/hour.

SECTION III

INTRODUCTION

In the previous section on performance details of a single stage rotary gas absorber it was noted that the liquid surface formation leaving the rings was either jet-like or a film which finally disrupted by means of a short jet length into droplets. These formations were dependent on total liquid flow and rotor speeds and not affected to any great extent by gas flow.

It was thought that a study of absorption and desorption processes in a liquid jet technique might be of use in correlating the rotary absorber results as well as giving an insight into the actual mechanism of absorption on fresh liquid surfaces. Very little published work has appeared on jet absorption in spite of the possible advantages of such a technique over wetted wall and disc columns in establishing fundamental gas absorption theory. Jet absorption techniques are less prone to rippling effects, and also minimise the velocity gradients set up in the liquid phase of these other units by the presence of the solid underlayer. However, they do have the disadvantage of small interfacial/

interfacial area unless certain special nozzles are constructed to give large jet diameters.

All previous work on jets has shown that the "penetration" mechanism could be applied successfully to the absorption process because the mass transfer rates are highest at the shortest jet lengths, i.e., short contact times. Matsuyama[45] studied physical absorption in jet lengths and tried to correlate his results on the basis of the penetration theory. The results, although they were scattered, showed that the theory was probably applicable. Work by Rumford et al.[49] on carbon dioxide absorption in ammoniacal liquid jets also showed that mass transfer rates were higher at small jet lengths although there was no attempt to connect the results with the penetration theory. Recently Cullen and Davidson[46] working on carbon dioxide absorption in liquid jets correlate their results by means of the momentum analogy with jet hydrodynamics. Their rates of mass transfer are found to be inversely proportional to the square root of the exposure time and would apparently confirm the earlier theories of Higbie.[4]

The present investigation considers absorption and desorption/

desorption processes for the ammonia-air-water system and air-ammonium hydroxide system respectively. A more intensive study is made of the desorption system owing to the ease of establishing the effects of variables on mass transfer rates.

EXPERIMENTAL

The jet system used is shown in Fig. 34 which is almost self explanatory. A jet of liquid formed at a venturi form nozzle (to avoid local turbulence) and flowed down through the 2" dia. gas space into a deep paraffin seal. The liquid layer reforming under this seal was drawn off through a moveable lute vessel for sampling and analysis. The rate of liquid flow to the jet was controlled by a needle valve on the supply line from a constant head tank and measured by an orifice flow meter. The gas stream could be admitted at one of several gas ports, corresponding to the length of jet required. Again the total gas stream was metered by flow meter and controlled by a needle valve, drawing off from a laboratory supply at about 1.5 lbs./sq.in.ga. Alternatively hydrogen gas could be substituted for air with a cylinder reducing valve giving suitable discharge pressure/

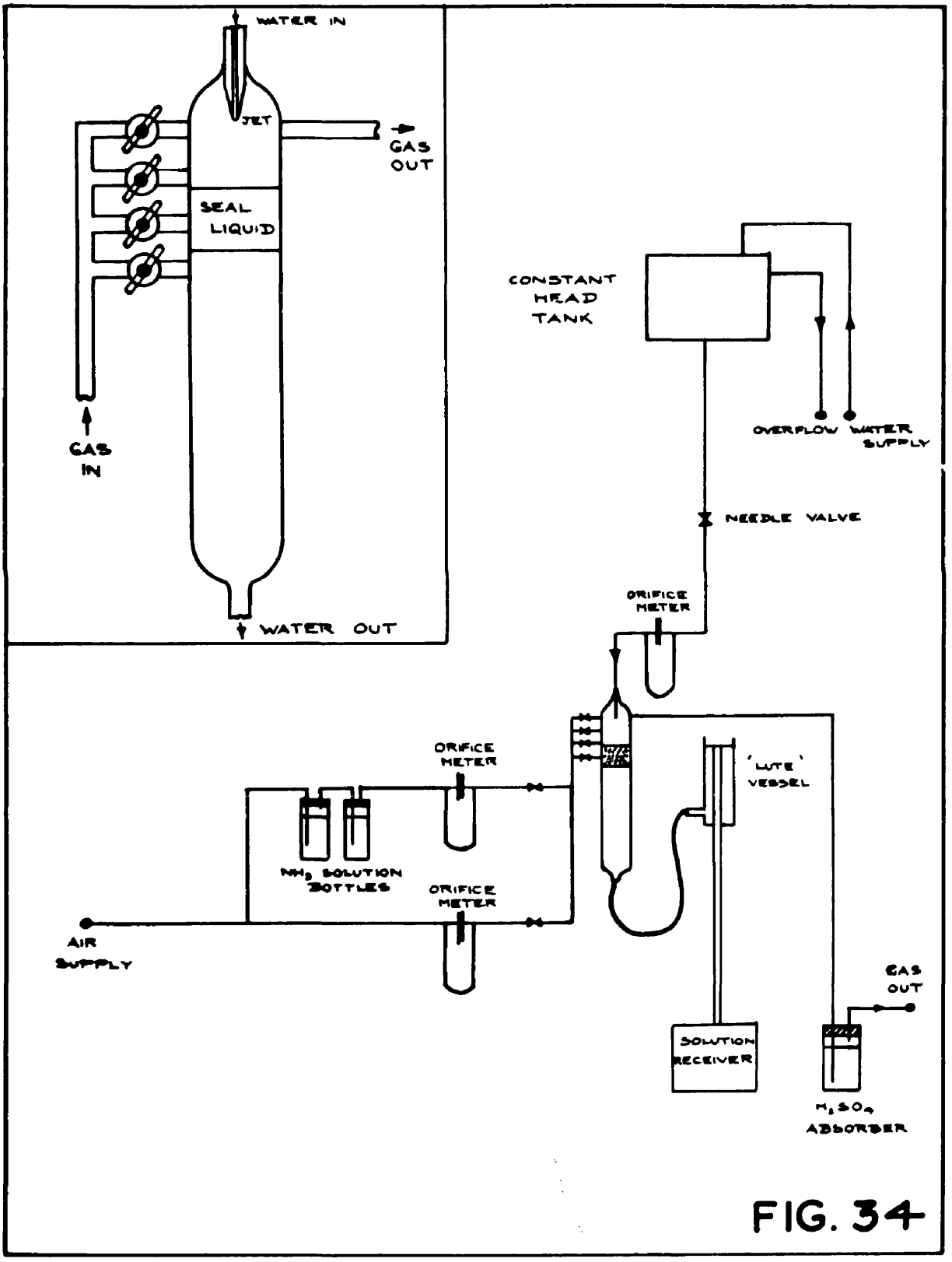

WATER IN
JET
GAS OUT
SEAL LIQUID
GAS IN
WATER OUT
CONSTANT HEAD TANK
OVERFLOW
WATER SUPPLY
NEEDLE VALVE
ORIFICE METER
ORIFICE METER
'LUTE' VESSEL
NH_3 SOLUTION BOTTLES
ORIFICE METER
AIR SUPPLY
SOLUTION RECEIVER
GAS OUT
H_2SO_4 ABSORBER

FIG. 34

pressure. In absorption tests a part of the air stream was byepassed direct to the absorption unit, with the remainder bubbling through ammonia saturating bottles. The two streams remixed before entering the jet chamber. Every effort was made to standardise ammonia concentration in all tests. In desorption tests the air went straight from meter to jet chamber.

Direct titration with sulphuric acid gave the ammonia concentration in the liquid phase, both in and out. The ammonia in the outlet gas stream was determined by passing the gas through absorption bottles containing 0.5 N sulphuric acid in excess. Determination of the excess acid by direct titration with the appropriate NaOH solution gave the ammonia content of the outlet gas. Methyl red was used as an indicator for all titrations. In the absorption tests, addition of ammonia contents for outlet liquid and outlet gas gave inlet gas concentration (only ammonia free water was used as inlet liquid). In desorption, the inlet - outlet conditions of the ammonia solution used were determined by titration. The ammonia in the air outlet stream was determined by noting the air volume required to neutralise a fixed amount of standard acid/

acid. The ammonia solution was held at approximately 2.02 N (inlet) with outlet conditions slightly lower (1.98 N). The usual amount of standard acid for the air stream measurements was 5 ml. of N/1 acid, contained in 300 ml. of water. This was sufficient for a run of 2 - 6 minutes, and accuracy of volume measurement was $\pm$ 2%.

In all experiments, the jet diameter was measured by a travelling microscope, and found to be substantially constant over the range of jet lengths used. The effect of surface tension depressants (anionic, cationic and non-ionic) on jet size under similar flow condition was inappreciable. As will be seen, they have some effect on the actual absorption.

In the preliminary absorption experiments the results of previous workers (Rumford et al) were checked by measurement of the effect of jet length, liquid velocity and liquid surface tension. All the new results are set out in Figs. 35, 36, 37, and 38, as plots of total absorption against the variables. The total absorption (lb.moles/ft^2.hr) was chosen rather than the mass transfer coefficient to compare more easily with earlier work.

In/

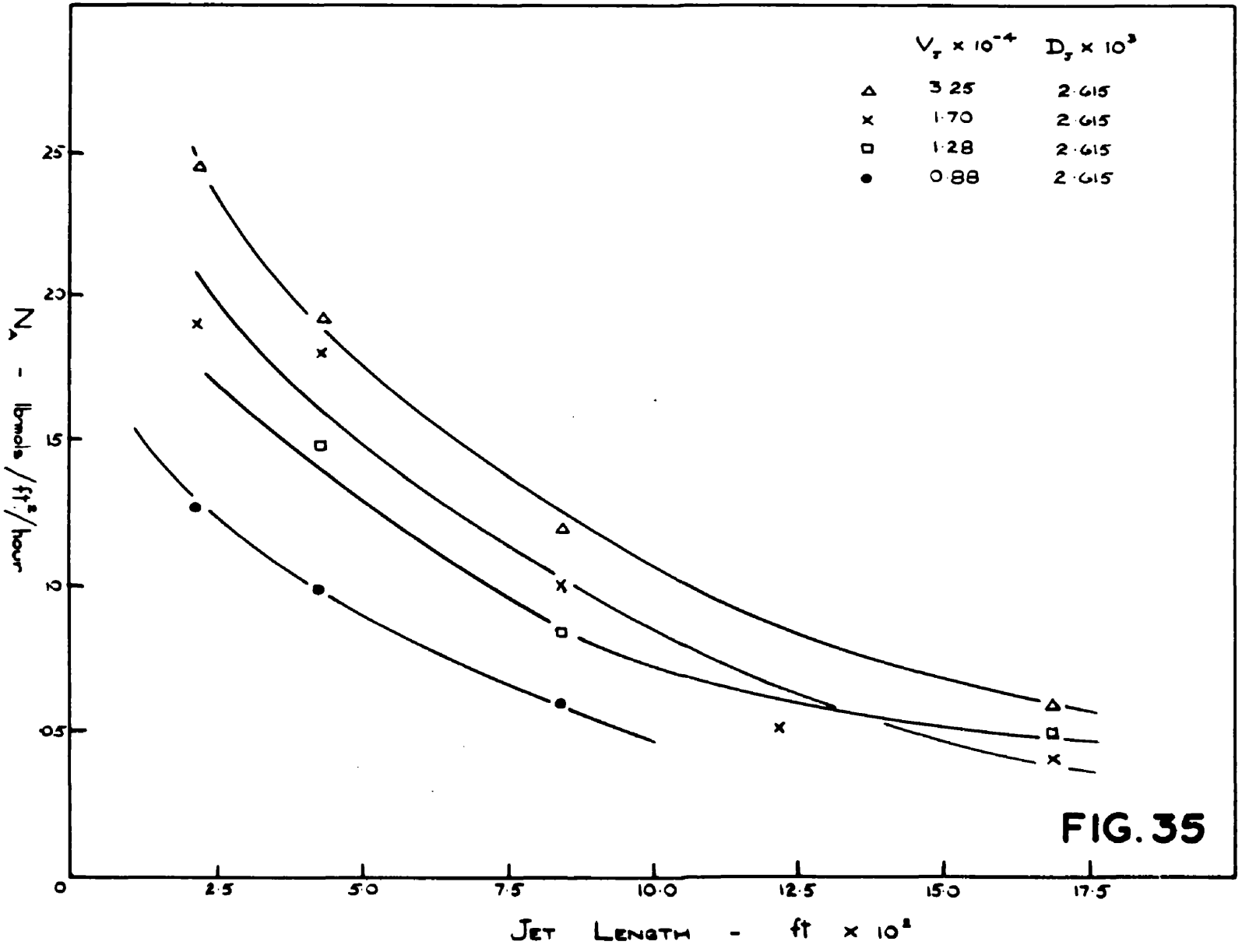

$V_r \times 10^{-4}$
$D_j \times 10^3$
△ 3·25 2·615
× 1·70 2·615
□ 1·28 2·615
● 0·88 2·615
N_v - lbmole/ft²/hour
0
0·5
1·0
1·5
2·0
2·5
2·5
5·0
7·5
10·0
12·5
15·0
17·5
Jet Length - ft × 10²

FIG. 35

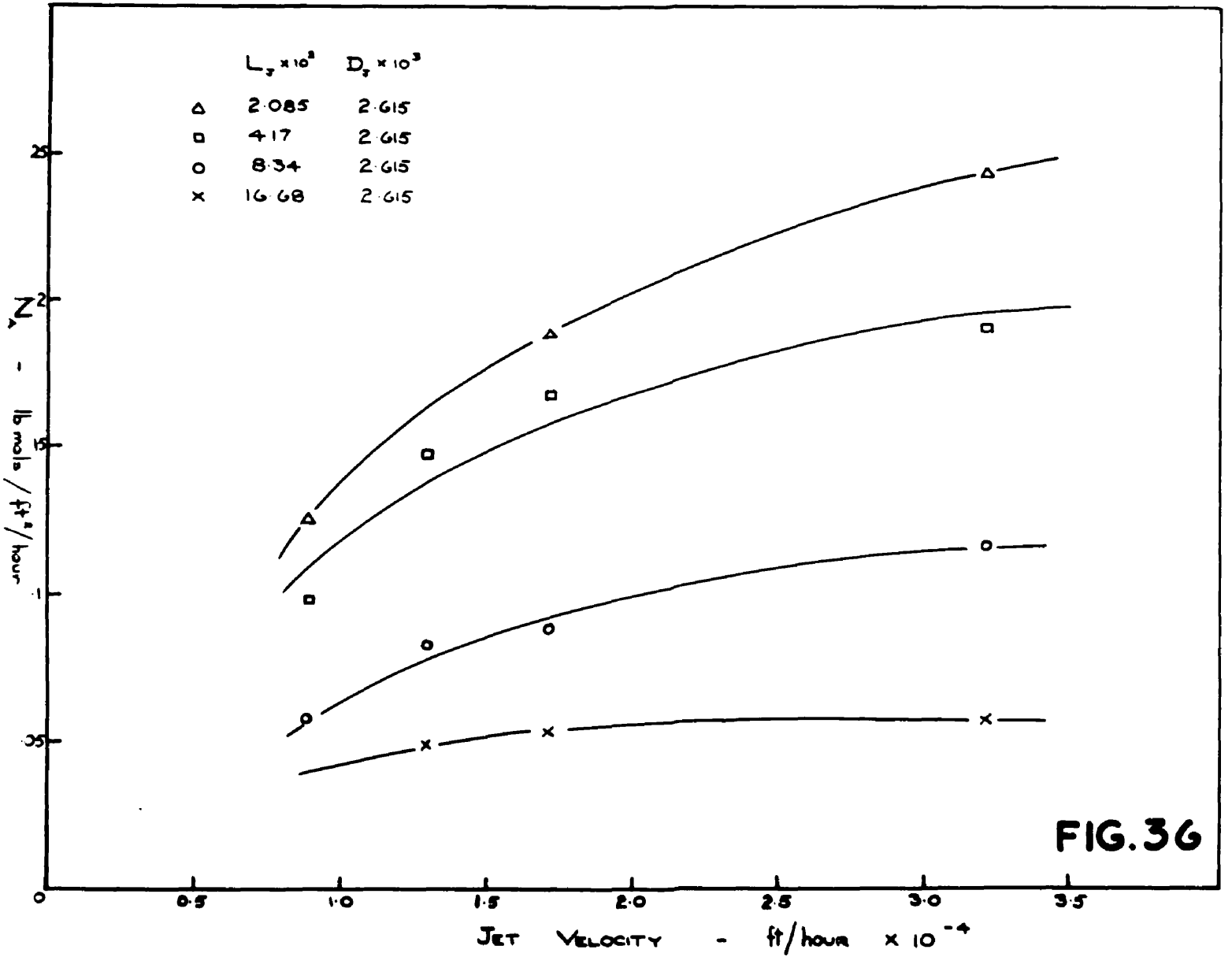

$L_y \times 10^3$ $D_y \times 10^3$
△ 2·085 2·615
□ 4·17 2·615
○ 8·34 2·615
× 16·68 2·615
N_A - lb mole / ft² / hour
2
1·5
1
·5
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
Jet Velocity - ft/hour × 10^{-4}

FIG. 36

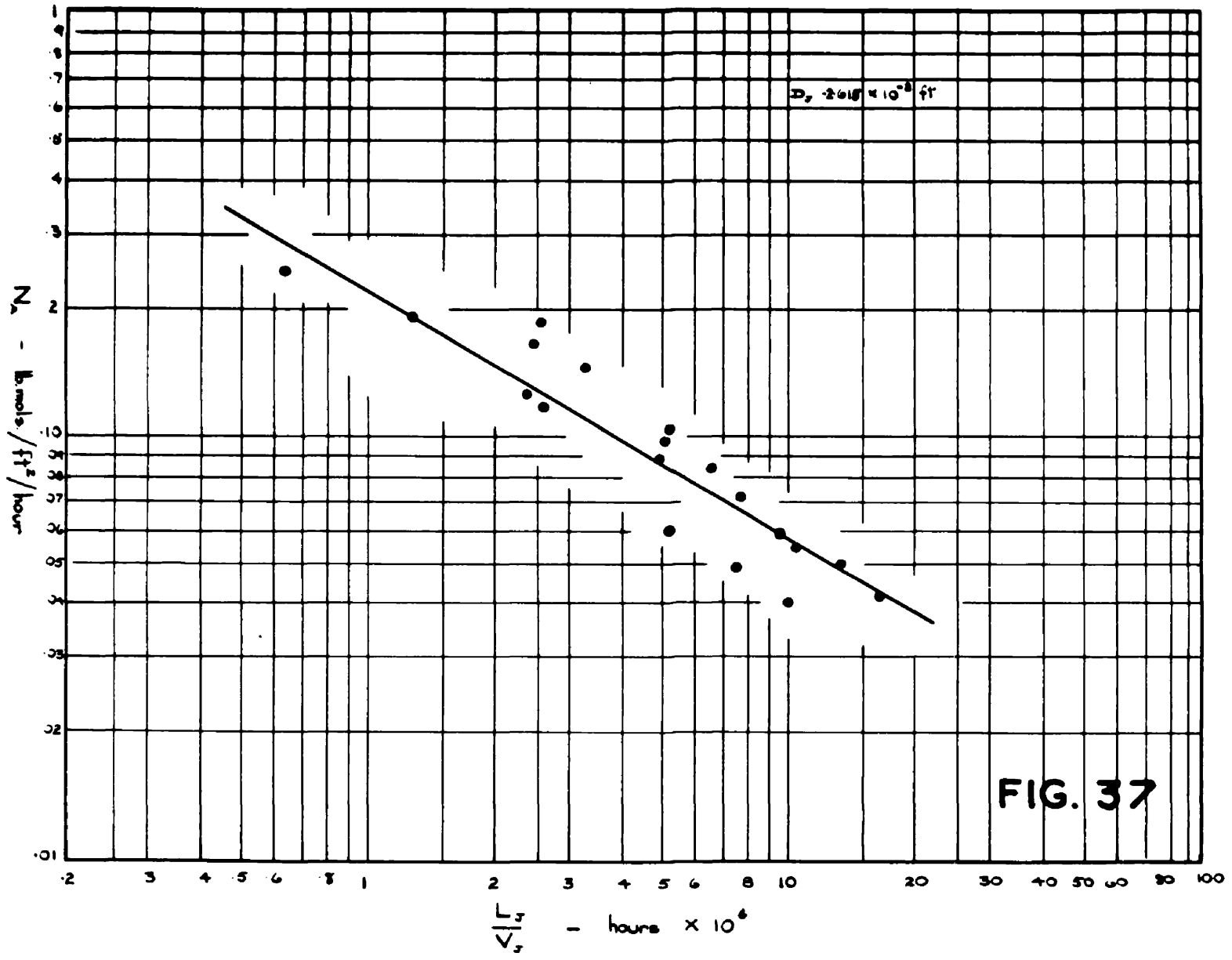

D_J = 2.615 × 10⁻⁵ ft²
N_A - lb.mols/ft²/hour
$\frac{L_J}{V_J}$ - hours × 10⁶
1
.9
.8
.7
.6
.5
.4
.3
2
.10
.09
.08
.07
.06
.05
.04
.03
.02
.01
.2
.3
.4
.5
.6
.8
1
2
3
4
5
6
8
10
20
30
40
50
60
80
100

FIG. 37

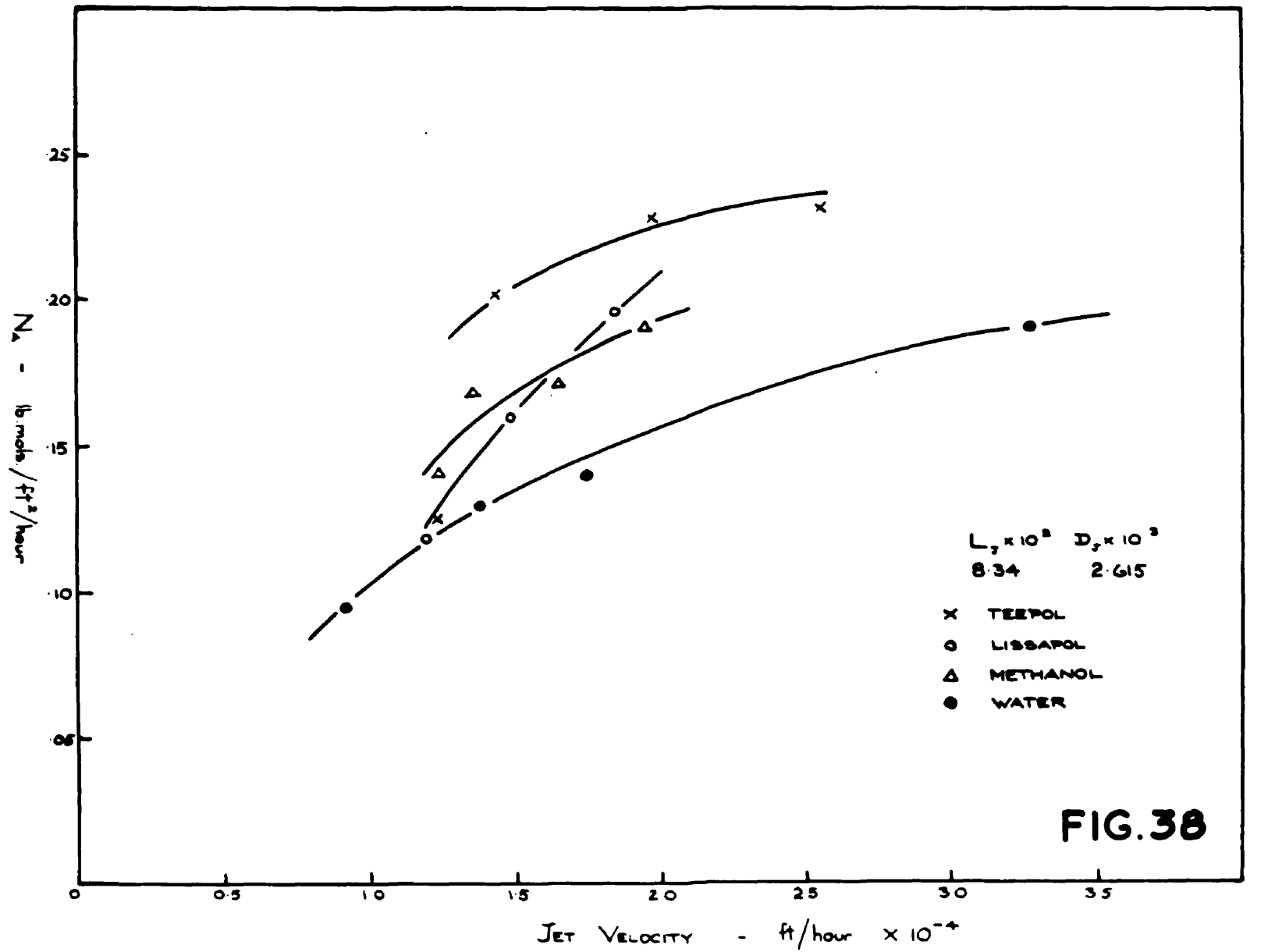

N_A - lb.mols/ft²/hour
.25
.20
.15
.10
.05
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
Jet Velocity - ft/hour × 10⁻⁴
$L_y \times 10^5$ $D_y \times 10^5$
8·34 2·615
× TEEPOL
o LISSAPOL
Δ METHANOL
● WATER

FIG. 38

In Fig. 35 the jet length is the variable and gives, for a standard jet and a series of liquid velocities, a family of curves of the form

$$N_a = a.L_j^{-b}$$

where b, the index of jet length, varies from 0.5 to 0.8.

In Fig. 36 the effect of varying liquid velocity while holding the jet length constant is shown in another series of curves in which

$$N_a = d.V_j^{c}$$

The curves of Figs. 35 and 36 can be compounded, as shown in Fig. 37. Here an apparent contact time (t_e) for the liquid film ($\frac{Lj}{Vj}$) is plotted against absorption rate. The equation of the mean line is

$$N_a = 0.000069\ t_e^{-0.585} \qquad (59)$$

The effect of surface tension, using Teepol, Lissapol and Methanol as depressants, are set out in Fig. 38. As will be seen the effects are small at best, a drop in surface tension of 50% only increases absorption rates from 0.17 to 0.23 (lb.moles/ft^2/hr.)

DISCUSSION/

DISCUSSION OF ABSORPTION RESULTS

First observations on Figs. 35 - 37 suggest that there is evidence supporting the Higbie-Danckwerts mechanism in that fresh liquid surfaces absorb more than "aged" surfaces. These rates of absorption when plotted against as apparent contact time (calculated from L_j and V_j) between gas and liquid, agree reasonably well with the Higbie-Danckwerts basic theory that the rate is inversely proportional to the square root of the contact time. An index of 0.585 instead of 0.5 is suggested as the function of the apparent contact time. However, it is appreciated that this calculated contact time may be very different from the true value, as it is doubtful whether the surface layer will have a uniform age distribution. Eddying of the surface caused by friction with the gas, or interior liquid drag, may vary up and down the jet. The interior of liquid jets has been shown to be in laminar[49] flow, up to R_e values of about 3000, by means of coloured streams, but turbulence of the actual surface layers due to the eddying, etc., is difficult to assess. It may be that the liquid as it leaves the tip of the glass jet has/

has its surface layers distributed, by surface tension changes or by the persistence of turbulence caused by a liquid drag on the sides of the glass jet (this may appear as rippling of the liquid surface).

The fundamental equation of the Higbie-Danckwerts mechanism is given as

$$N_a = (c_e - c_o) \cdot 2\sqrt{D_L/t_e \cdot \pi} \qquad (60)$$

for this case of ammonia absorption we have $D_L = 6.8 \times 10^{-5}$ ft^2/hr.[68] and $(c_e - c_o) = 0.55$ lb.mol/ft^3.[68] Substituting in Eq. (60) gives

$$N_a = 0.00515\ t_e^{-0.5} \qquad (61)$$

The above equation assumes the liquid at the interface to be in equilibrium with the gas. Comparing Eqs. (59) and (61) it is noticed that the experimental equation gives normally much smaller rates than those predicted from Eq. (60).

The results shown in Fig. 38 are confusing. There has been appreciable increase in absorption rate with some of the surface active agents, teepol in particular. This contradicts the suggestion that a reduction in absorption/

absorption rate might be expected due to the suppression of rippling effects, and the presence of long chain molecules at the interface. The latter can be ruled out on the basis of work by Addison[48] who has shown that it requires longer than 1/100th of a second for molecules of surface active agents to orientate themselves at the surface of liquid jets. In the present work the life of the jets is in the region 0.06 - 0.002 seconds. The nature of the surface active agents, i.e., whether anionic, cationic or non-ionic does not seem to follow any rule as regards affecting absorption rates.

DESORPTION EXPERIMENTS

As indicated above, the absorption tests were the prelude to a wider range of desorption work in which the ammonia was removed from liquid solutions by a gas stream. In view of the very rapid change in partial pressure of NH_3 over aqueous solutions with temperature and concentration it was decided to standardise liquid concentration as nearly as possible at 2N (34 gms. NH_3 per litre of solution) and to apply a temperature correction to all tests. This correction was made empirically from the data set out in Fig. 39, and/

and all later results were corrected back to a basic temperature of 20°C (inlet solution temperature). In retrospect it would probably have been better to mount the whole absorption system in a large thermostatic tank and control the inlet temperature but no suitable tank was available at the time.

The first variable investigated was liquid velocity, the effects of which on desorption rate are shown in Fig. 40. It is apparent from this graph that the diameter of the jet also influences the desorption rate. In Fig. 41 the possibility of turbulence effecting the mass transfer rates is shown as a plot of R_e (for the jet) against desorption rate. An interesting comparison with the absorption process is also shown; the absorption was with a jet of .0834 ft. length and 2.615×10^{-3} ft. diameter.

Fig. 42 shows the effect of variation in gas flow (range 0.25 - 3.00 ft^3/hr.) on desorption rate at different jet lengths. This may be misleading in view of large variation in the outlet gas concentration. In order to assess the actual gas phase conditions that are present in the desorption tube, Fig. 43 shows a plot of exit gas concentration against desorption rate.

The/

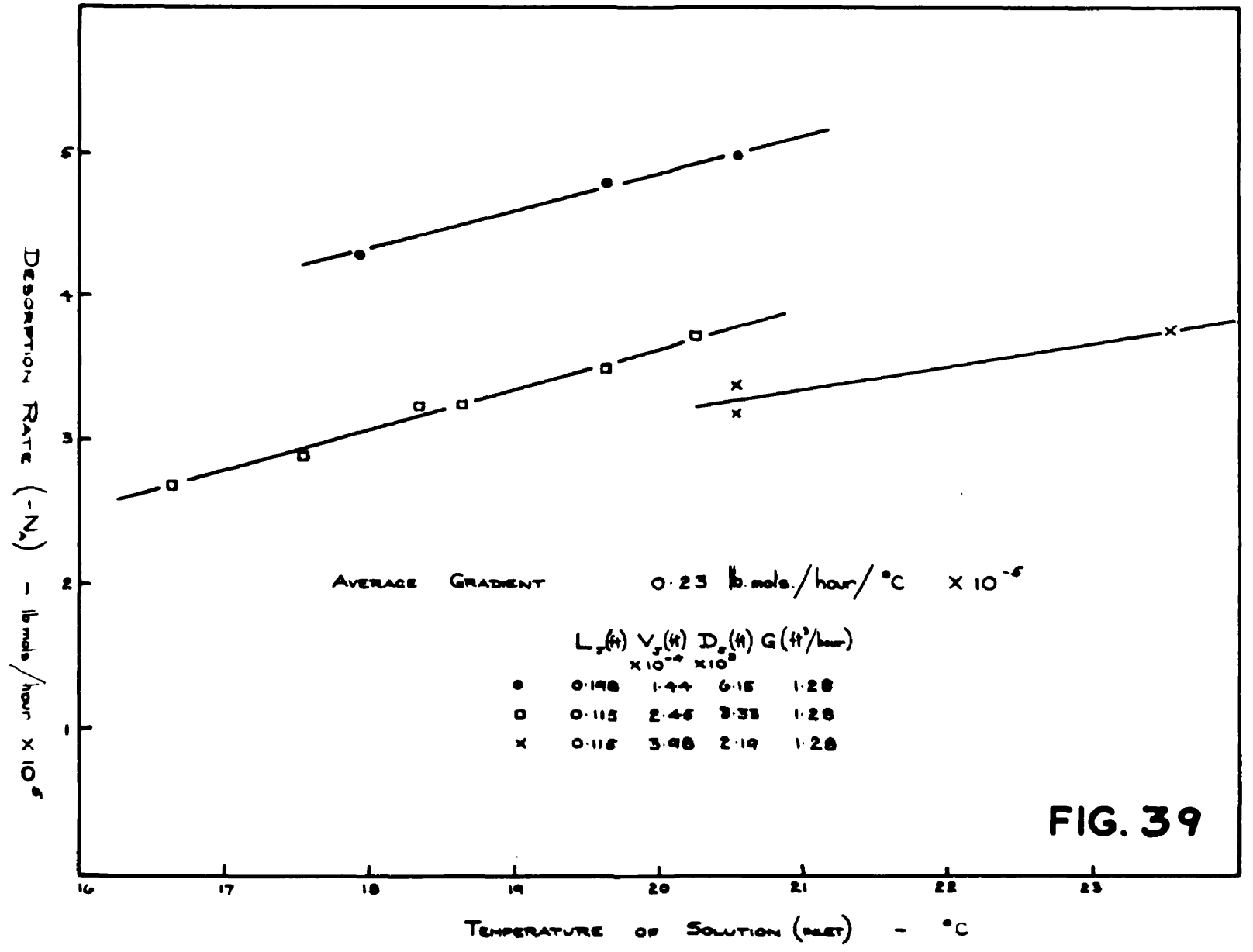

Desorption Rate ($-N_A$) - lb mols/hour x 10^{-6}
Temperature of Solution (inlet) - °C
16
17
18
19
20
21
22
23
1
2
3
4
5
Average Gradient 0·23 lb. mols./hour/°C x 10^{-6}
L_g(ft) V_g(ft) x 10^{-4} D_g(ft) x 10^{3} G(ft³/hour)
● 0·198 1·44 6·15 1·28
□ 0·115 2·46 3·33 1·28
× 0·116 3·98 2·19 1·28

FIG. 39

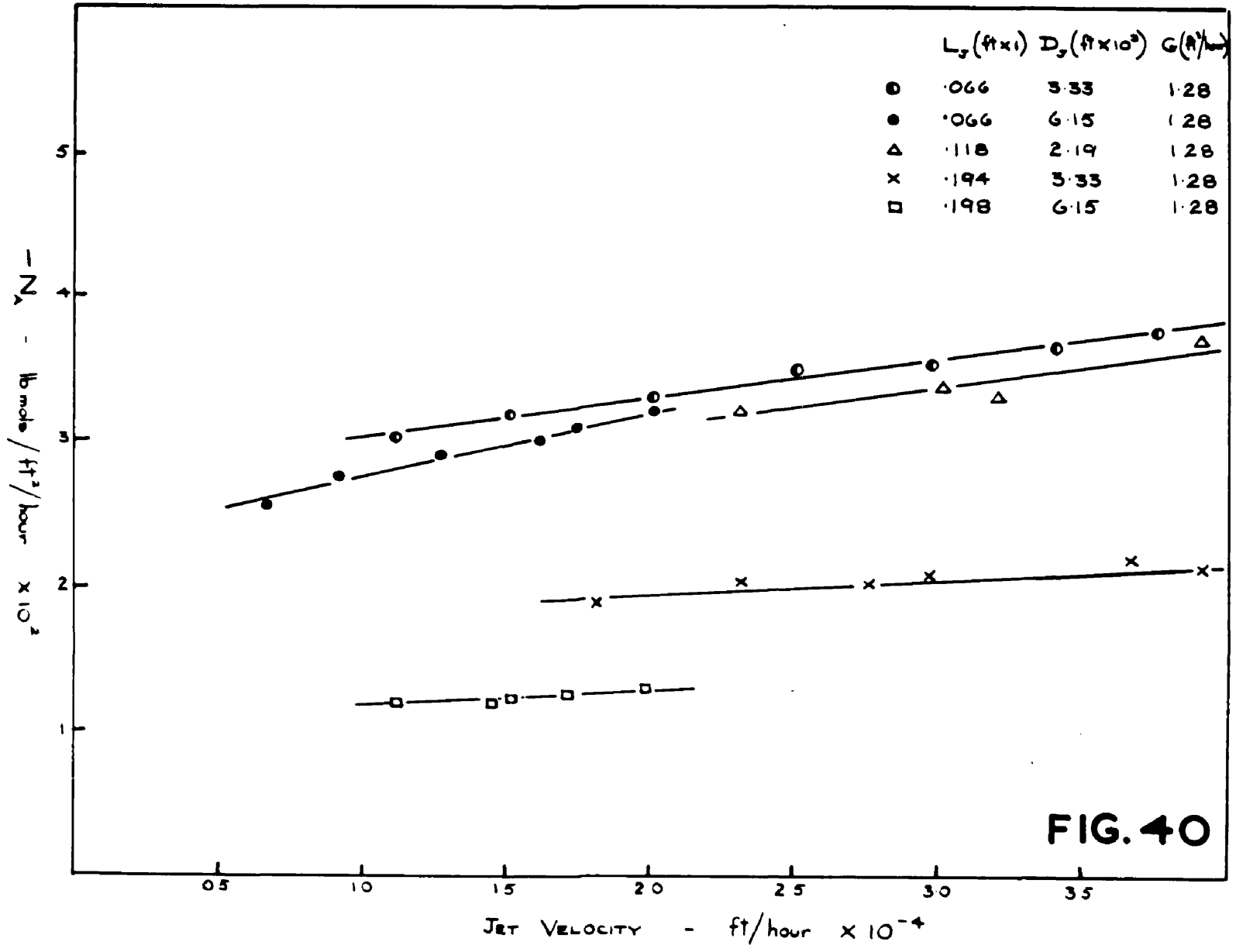

L_y (ft x 1) D_y (ft x 10^5) G (lb/hr)
· 066 3·33 1·28
· 066 6·15 1·28
· 118 2·19 1·28
· 194 3·33 1·28
· 198 6·15 1·28
N_x - lb mole / ft² / hour x 10^2
1
2
3
4
5
05
10
15
20
25
30
35
Jet Velocity - ft/hour x 10^{-4}

FIG. 40

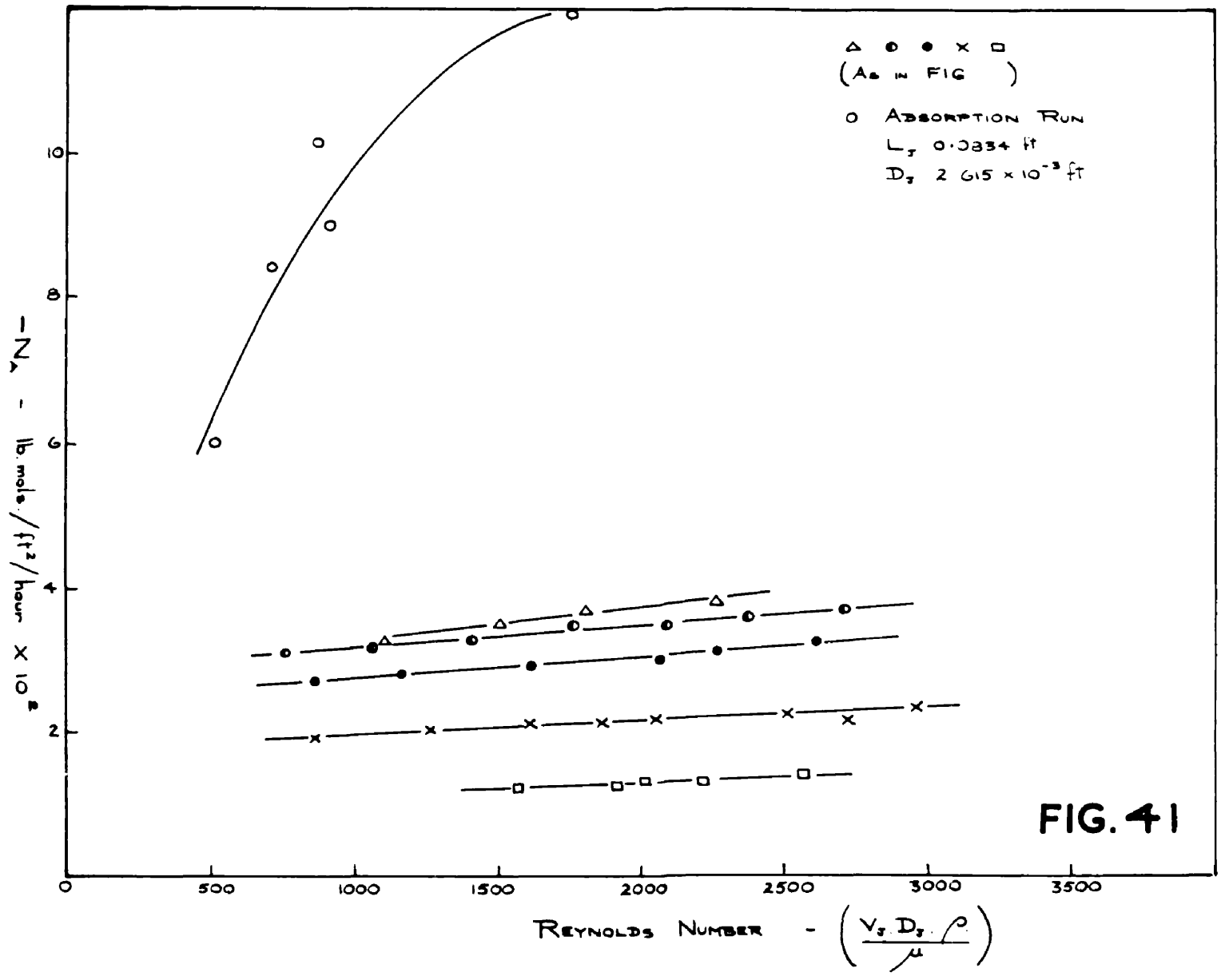

△ ◐ ● × □
(As in FIG)
o Absorption Run
L_J 0.0834 ft
D_J 2 615 × 10⁻³ ft
N_A - lb. moles/ft²/hour X 10³
0
2
4
6
8
10
500
1000
1500
2000
2500
3000
3500
Reynolds Number - $\left(\frac{V_J \cdot D_J \cdot \rho}{\mu}\right)$

FIG. 41

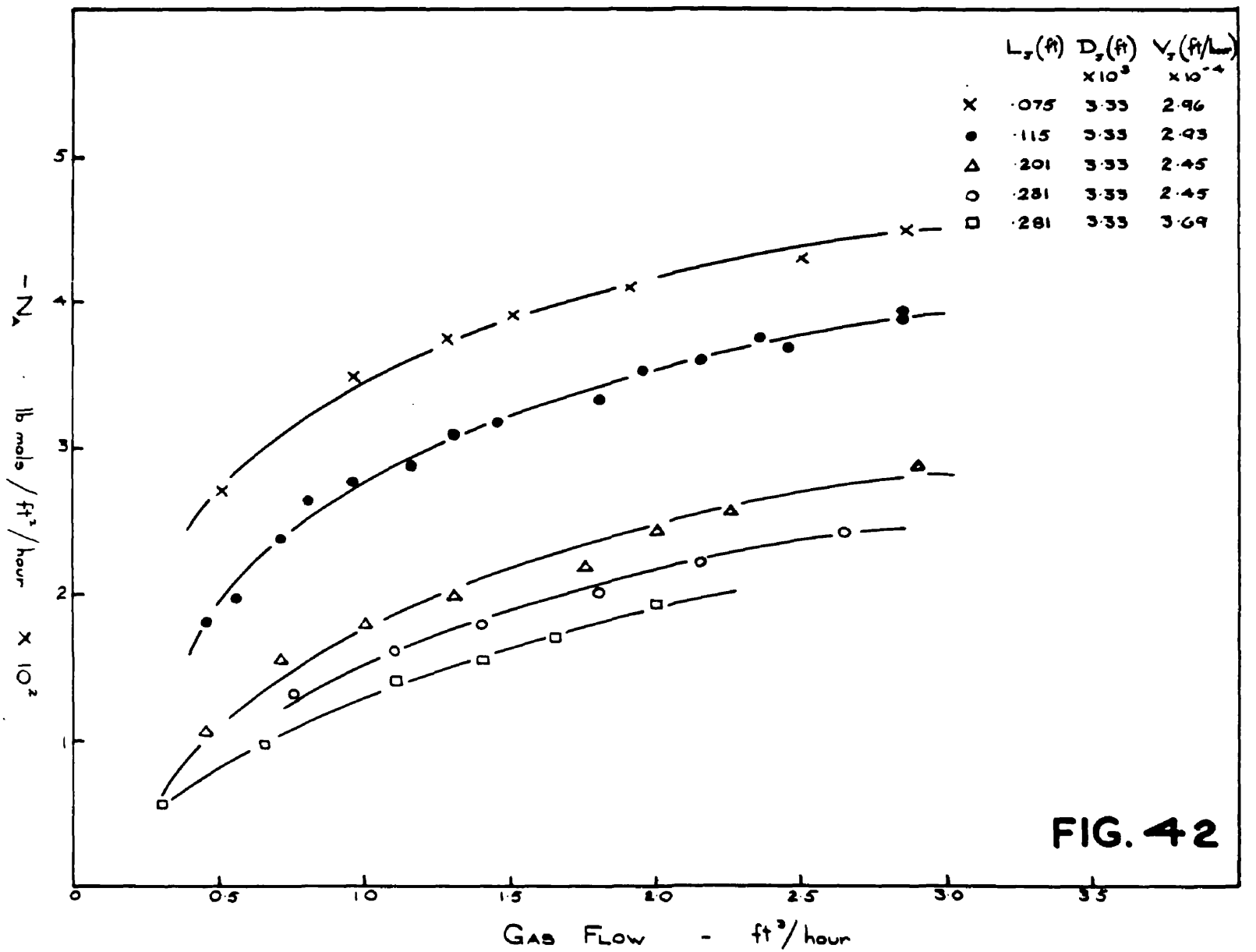

L_z (ft)
D_z (ft) x10^{3}
V_z (ft/hour) x10^{-4}
× ·075 3·33 2·96
● ·115 3·33 2·93
△ ·201 3·33 2·45
○ ·281 3·33 2·45
□ ·281 3·33 3·69
$-N_A$ lb mols / ft^2 / hour x 10^2
0 0·5 1·0 1·5 2·0 2·5 3·0 3·5
1 2 3 4 5
Gas Flow - ft^3/hour

FIG. 42

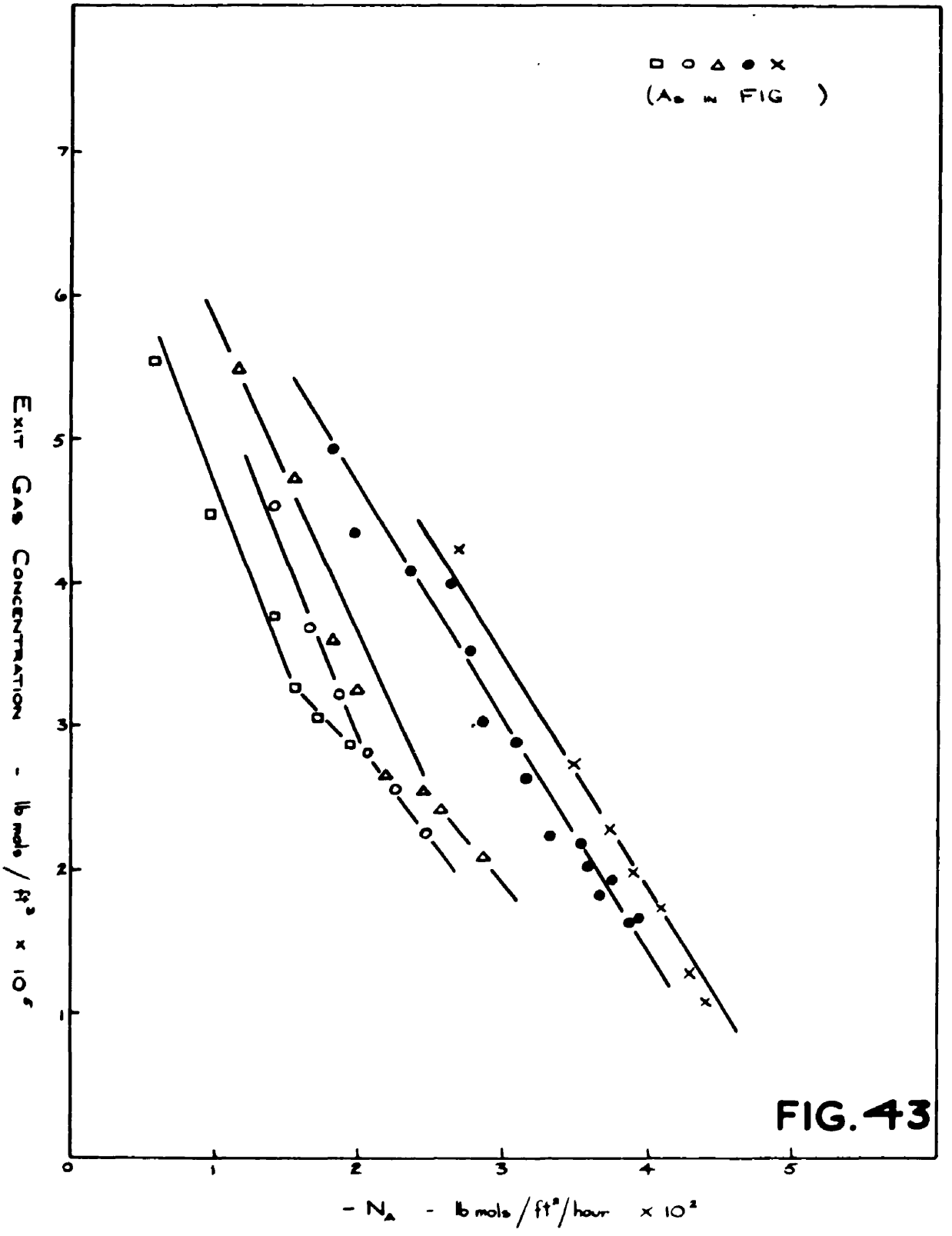

□ ○ △ ● ×
(As in FIG)
Exit Gas Concentration - lb mols / ft³ x 10⁶
- N_A - lb mols / ft² / hour x 10²
0
1
2
3
4
5
6
7

FIG. 43

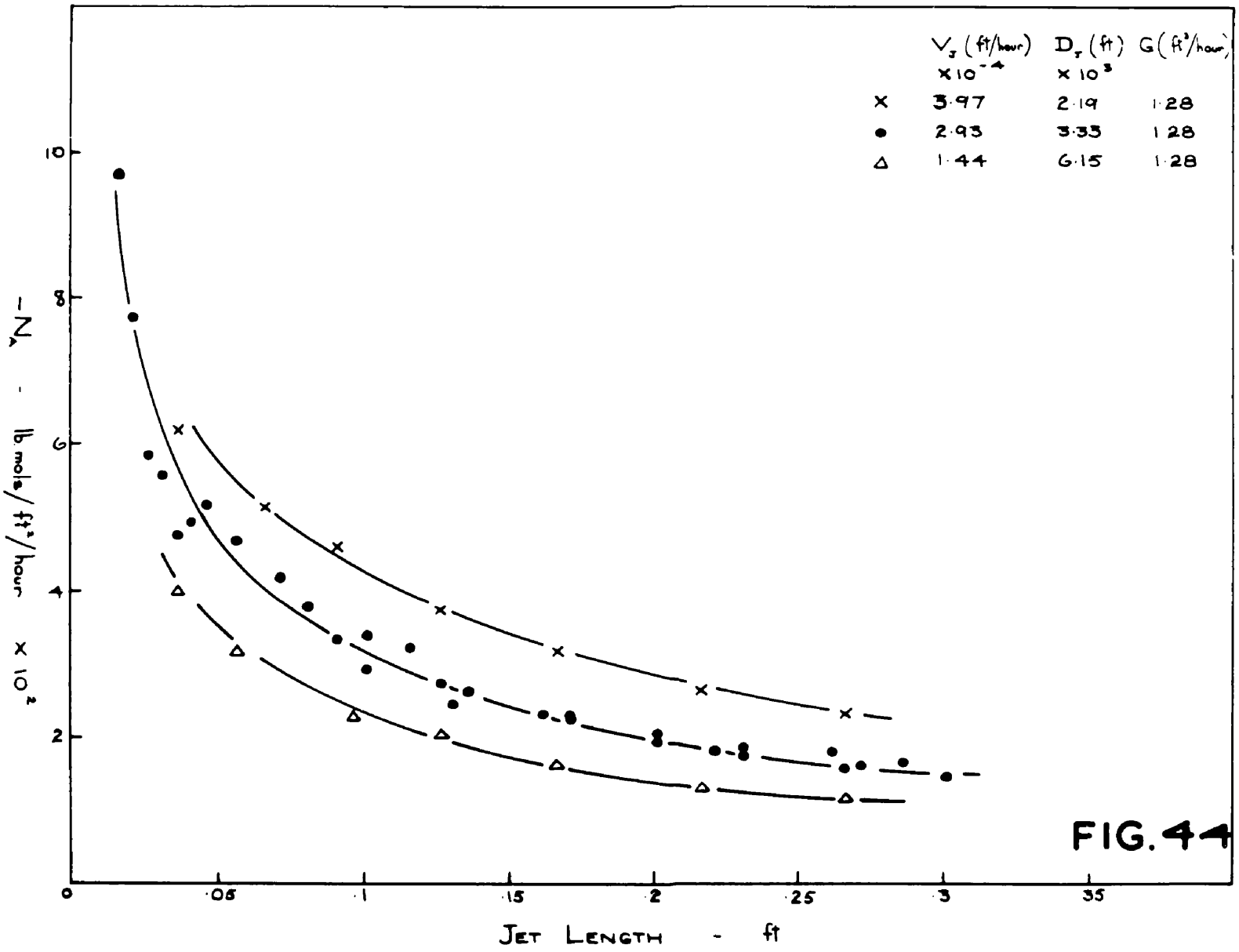

V_j (ft/hour) $\times 10^{-4}$
D_j (ft) $\times 10^3$
G (ft³/hour)
× 3·97 2·19 1·28
● 2·93 3·33 1·28
△ 1·44 6·15 1·28
$-N_A$ - lb mole/ft²/hour × 10^2
10
8
6
4
2
0
·05
·1
·15
·2
·25
·3
·35
Jet Length - ft

FIG. 44

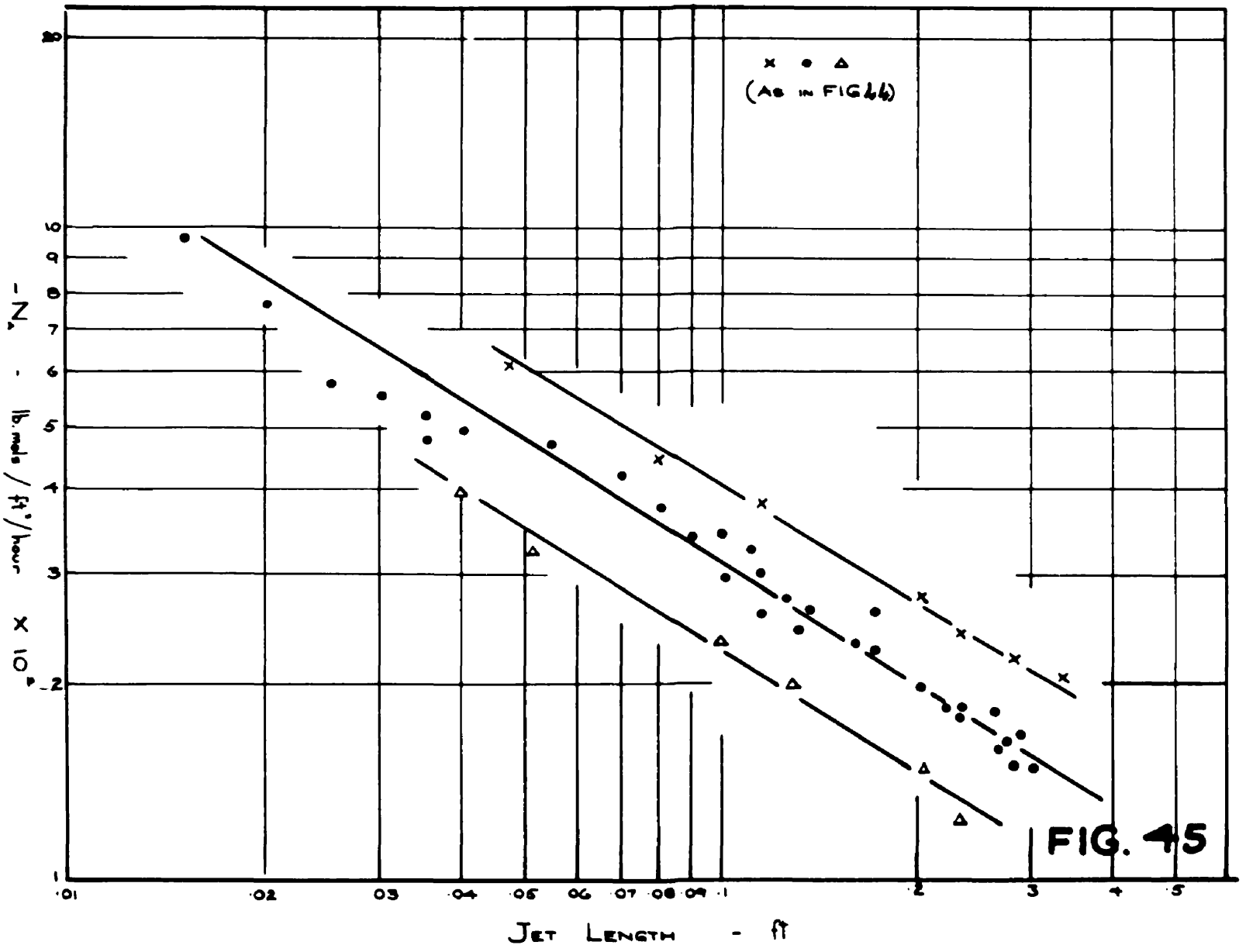

× ● △
(As in FIG 44)
N_r - lb. mols / ft.² / hour x 10^{-2}
10
9
8
7
6
5
4
3
2
1
·01
·02
·03
·04
·05
·06
·07
·08
·09
·1
·2
·3
·4
·5
Jet Length - ft

FIG. 45

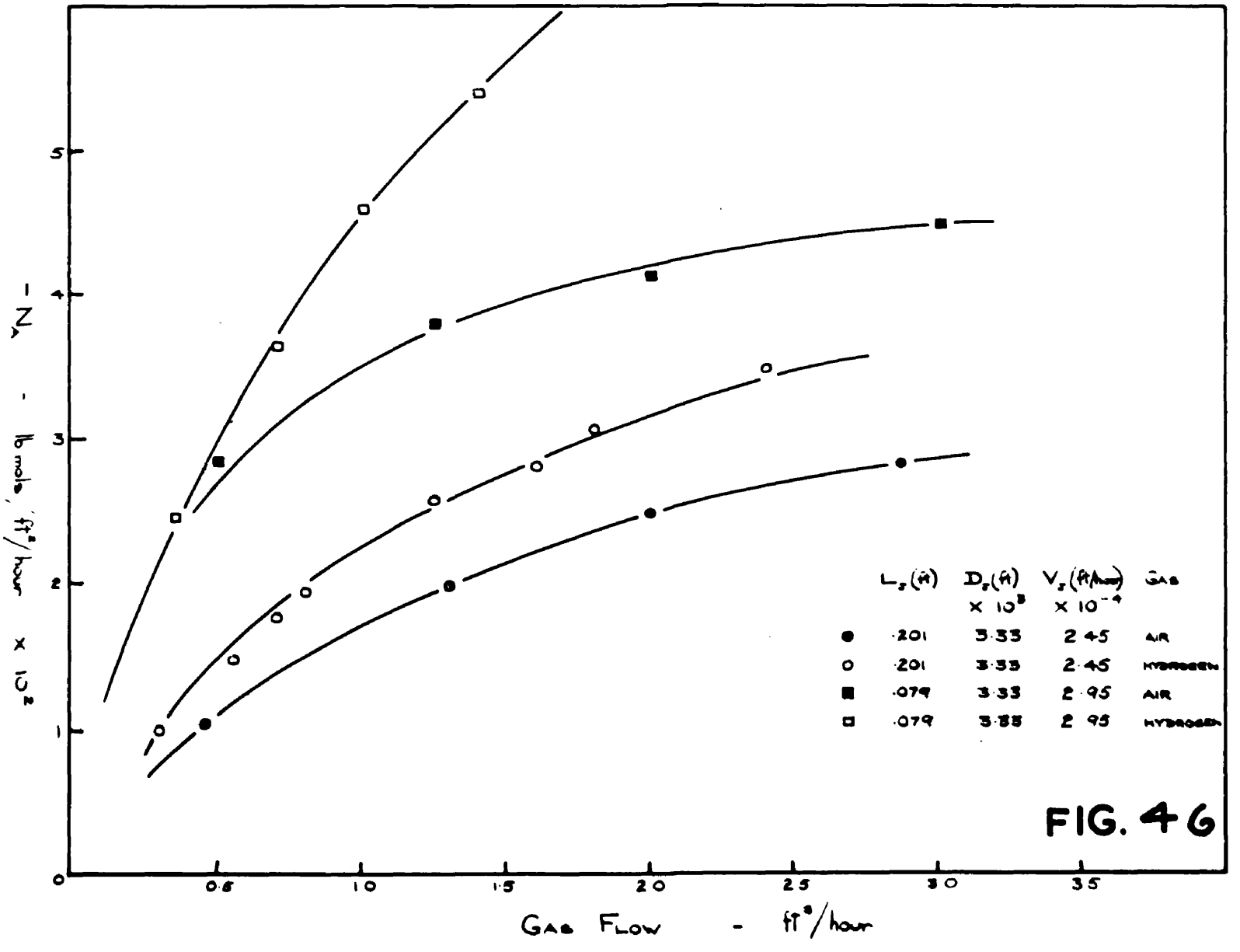

N_A - lb moles/ft² hour x 10²
0
1
2
3
4
5
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Gas Flow - ft³/hour
L_s(ft) D_s(ft) × 10⁵ V_s(ft/hr) × 10⁻⁴ Gas
● .201 3.33 2.45 AIR
○ .201 3.33 2.45 HYDROGEN
■ .079 3.33 2.95 AIR
□ .079 3.33 2.95 HYDROGEN

FIG. 46

The effect of jet length on desorption rate is shown in Fig. 44. These curves are better set out on log-log paper, as in Fig. 45. The line drawn through the points for G = 1.28 ft^3/hr, D_j = 3.33 x 10^{-3}ft. and V_j = 2.93 x 10^4 ft/hr. has the general equation

$$N_a = .0075\ L_j^{-0.62} \qquad (62)$$

A few tests were carried out with hydrogen instead of air as the desorbing gas. The results are set out in Fig. 46.

DISCUSSION OF DESORPTION RESULTS

The effect of temperature changes on the desorption process had been noted as a large factor in determining actual rates. Thus over the range, 16 - 24°C, a coefficient was established which would allow all the results to be assessed on a temperature basis of 20°C. This coefficient is given as 0.23 lb./mols./hr./°C - a figure compiled from the average gradients of the curves of Fig. 39.

From Fig. 40, an increase in liquid velocity from 0.6 x 10^4 ft./hr. to 4.2 x 10^4 ft./hr. at various jet lengths and diameters results in a slight increase in the/

the desorption rate. These curves, as they do not appear to pass through the origin, indicate that there will be end effects produced at the jet tip, or that the desorption rate increases rapidly over the range of jet velocity 0.- 0.5 ft./sec. Obviously at very low rates of flow a jet will not form. There is also a slight increase in desorption rate as the jet diameter is decreased, which would suggest some enhanced non laminar flow in the outer layers of the jet liquid. This effect contradicts the work of Rumford et al[49] who found the absorption rate of carbon dioxide in ammonium hydroxide increasing with increased jet diameter at a constant jet velocity, i.e., with an increase in Reynolds Number.

If the results from Fig. 40 are plotted as Reynold's numbers versus desorption rate (see Fig. 41) it is seen that desorption rates are almost independent of normal criteria of turbulence. This is very different from absorption, but it might have been interesting to investigate very low values of the Reynold's Number. Unfortunately a jet is seldom stable under these conditions.

It can be briefly stated then, that the effects of/

of the physical properties of the jet on desorption rate are (a) slight increase with liquid velocity over the range of values covered (b) slight increase with jet diameter and (c) almost complete dependence on jet length. The first conclusion is the more surprising when it is considered that the absorption results do not follow this rule. Fig. 41 indicates this non-conformity of the two processes by showing that the absorption rate increases rapidly with increase in liquid R_e values whereas the desorption rate remains almost unaffected over the same range.

This anomaly may be due to the larger concentration head in the absorption case (almost five times as much in desorption). However, it is still apparent that there must be a rapid decrease in desorption rate at lower R_e values if the curves are to pass through the origin. There is every indication that the absorption curve will pass through the origin.

A certain minimum velocity is required in order that a stable jet be formed. This in turn requires a fixed liquid surface from which desorption will occur - most rapidly with the fresh surface. This rate is curiously unaffected by liquid conditions,

and/

and suggests almost complete dependence on gas film transfer.

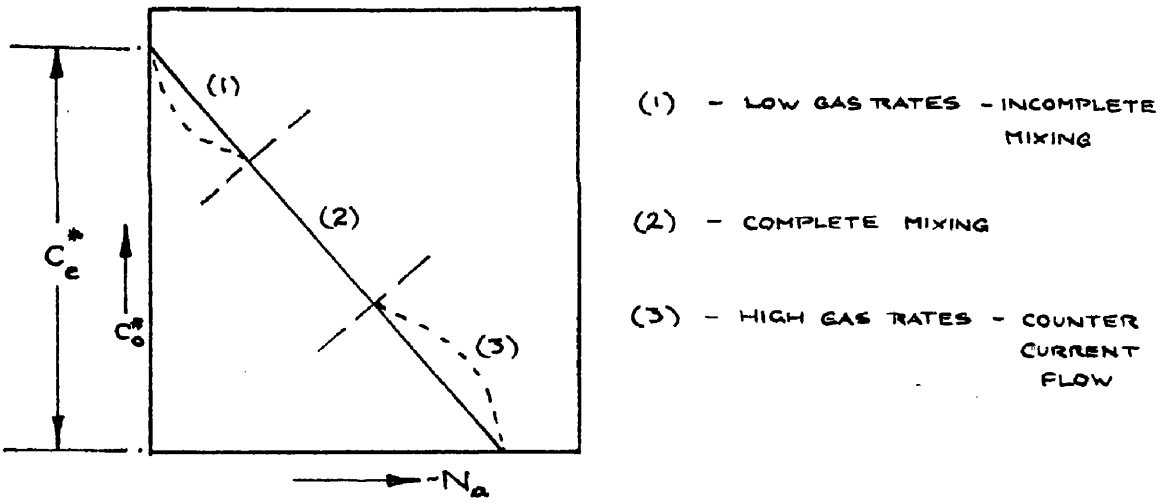
Fig. 42 shows the effects of gas rate on desorption and as might be expected increased gas rates result in a considerable increase in N_a. The graph also shows that desorption rates are higher at the shorter jet lengths. These curves illustrate the dependence of the ammonia desorption on gas film conditions. It appears that there is an ample supply of ammonia molecules present at the interface, and increased gas rates sweep these away in increasing quantities. As the gas flow is not nearly turbulent (R_e 50 - 250) it is improbable that the increased desorption rates are due to gas disturbed liquid surfaces. Indeed, in view of the approximate value of the gas residence time (chamber volume/gas rate - of the order of 10 seconds) it is possible to suggest complete mixing of the gas in the chamber. From Fig. 43, a plot of exit gas concentration against desorption rate, the intercepts of the graphs on the concentration axis are almost the same in each case. This value agrees very well with the value for the concentration of ammonia in the gas phase in equilibrium with 2N ammonia hydroxide/

hydroxide solution[68] and suggests that mixing in the chamber is complete in all the tests carried out. If this is correct the equations of the curves on Fig. 43 take the form (see diagram below)

$$N_a = K_G(c_e^* - c_o^*) \qquad (63)$$

c_o^* = exit gas concentration - lb.mols./ft^3

c_e^* = equilibrium concentration in gas - lb.mols./ft^3



This equation is identical with the equation derived from the "film concept" with K_G representing the overall mass transfer coefficient and $(c_e^* - c_o^*)$ the concentration head due to complete mixing in the system. Thus K_G values for each line (given by the gradient) show independence of gas rates and only vary with jet length. At higher gas rates the equation will/

will not hold due to the onset of a counter current flow pattern. Some of the curves indicate this tendency by a tail effect. With low gas rates the mixing will be incomplete with stagnant sections and channelling occuring thus causing the curve to fall below the Eq. (63) line. (See diagram above).

Now a "gas mixing" phenomenon of this type will show dependence of absorption on gas velocity, but it is only a concentration effect. Large quantities of gas keep the exit concentration low and the value of $(c_e^* - c_o^*)$ high. There is no question of increased turbulence, or of change in the physical gas film conditions. However, such a change might take place, and the matter was further investigated by substituting hydrogen for air as the "sweeping" gas.

Results, as shown in Fig. 46, certainly show a greater rate of desorption, and can be taken as an indication, not conclusive, that the gas film controls.

Now D_G for air-ammonia is given as 0.90 $ft^2/hr.$ and D_G for hydrogen-ammonia, calculated from Gillilands formula[69], is 2.3 $ft^2/hr.$ These two diffusion coefficients indicate that the ammonia should be desorbed about twice as fast through the hydrogen than/

than through the air. From a liquid side resistance theory the rate should be unchanged. This is taken as further proof of gas film control for desorption of ammonia from water.

The effect of jet length in absorption rate is shown in Fig. 44. It is again evident, as with absorption results, that mass transfer rate increases with decrease in jet length. Over the range of jet lengths used the equation of the middle curve (specified above) is given by

$$N_a = 0.0075\ L_j^{-0.620} \qquad (64)$$

The other curves have similar indices but the constant 0.0075 varies with the change in jet diameter and velocity and gas rate.

Again, as with absorption, the principal variable is the jet length.

If, as with the absorption results, the jet velocity and jet lengths are compounded as L_j/V_j ans plotted against K_G (K_G being calculated from $N_a/(c_e^* - c_o^*)$ - then from Fig. 47, which shows the plot of all the experimental desorption results, as well as absorption runs, it is found that the relationship/

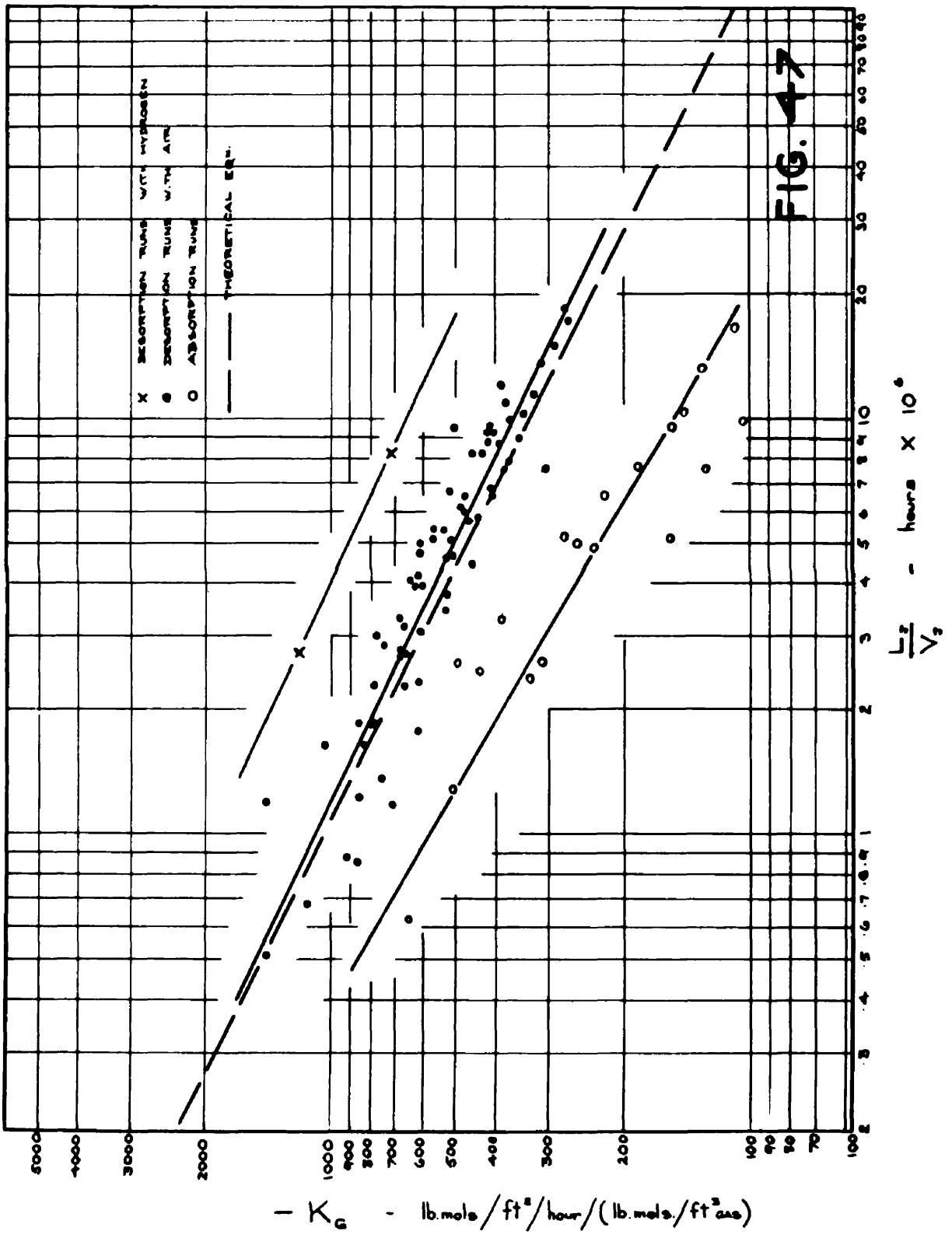


FIG. 47
DESORPTION RUNS WITH HYDROGEN
DESORPTION RUNS WITH AIR
ABSORPTION RUNS
THEORETICAL EQN.
$\frac{L_2}{V_2}$ - hours × 10^4
$-K_G$ - lb.mole/ft²/hour/(lb.mole/ft³atm)

relationship between the two parameters K_G and L_j/V_j is a straight line on log-log paper.

The equation of the best line through the points is given as

$$K_G = 1.35 \left(\frac{L_j}{V_j}\right)^{-0.485} \qquad (65)$$

Now the parameter (L_j/V_j) can be identified with the apparent contact time of the phases, t_e. Thus

$$K_G = 1.35\ t_e^{-0.485} \qquad (66)$$

For the absorption results the equation of the line through the points, although it cannot be so definite due to the scattering, is given as

$$K_G = 0.177\ t_e^{-0.585} \qquad (67)$$

For the hydrogen tests (only two results) the equation of the line is

$$K_G = 2.42\ t_e^{-0.48} \qquad (68)$$

These results will now be compared with the penetration theory based on liquid diffusion. It is obvious that the Whitman theory would not show any dependence on contact time.

From/

From the Higbie conception

$$N_a = (c_e - c_o) \cdot 2\sqrt{\frac{D_L}{\pi . t_e}}$$

Thus

$$K_L = \frac{K_G}{H} = \frac{N_a}{(c_e - c_o)} = 2\sqrt{\frac{D_L}{\pi . t_e}}$$

$$\therefore \quad K_G = H.2.\sqrt{\frac{D_L}{\pi . t_e}}$$

$$\therefore \quad K_G = 13.9\ t_e^{-0.5} \qquad \text{(69)}$$

Then calculation based on liquid film penetration is not in good agreement with the experimental work. Now it must be remembered that the process is apparently under gas film control.

If the Higbie concept holds for all fluids, i.e. gas or liquid, then an application of this concept to a semi infinite gas will give a standard diffusion equation.

$$\frac{\partial c^*}{\partial t} = D_G \cdot \frac{\partial^2 c^*}{\partial x^2} \qquad \text{(70)}$$

D_G is assumed constant, heat effects and expansion are neglected and the gas layer taken as of infinite depth.

When/

When $c^* = c_o^*$, $x > 0$, $t = 0$

$c^* = c_e^*$, $x = 0$, $t \geqslant 0$

$c^* = c_o^*$, $x = \infty$, $t \geqslant 0$

Under these conditions the concentration is given by

$$c^* = c_o^* + \frac{c_e^* - c_o^*}{\sqrt{\pi . D_G t}} \cdot \int_x^{\infty} e^{-x^2/4D_G t} \cdot dx$$

Where F the amount of gas absorbed up to time t_e is

$$F = 2(c_e^* - c_o^*)\sqrt{\frac{D_G t_e}{\pi}}$$

$$\therefore \quad N_a = (c_e^* - c_o^*) \quad 2\sqrt{\frac{D_G}{\pi t_e}} \qquad \text{(71)}$$

(c^*, c_e^*, c_o^* are gas side concentrations of solute gas expressed in lb.mol./ft^3.gas.) This analysis assumes that the liquid film offers no apparent resistance.

On this basis the theoretical equation for absorption or desorption from or to a thoroughly mixed gas bulk to a liquid jet under the condition of the experiment is

$$\frac{N_a}{(c_e^* - c_o^*)} = 2\sqrt{\frac{D_G}{\pi . t_e}} = K_G$$

$$\therefore \quad K_G = 2\sqrt{\frac{0.90}{\pi . t_e}}$$

$$\text{i.e.} \quad K_G = 1.07\ t_e^{-0.5} \qquad \text{(72)}$$

This equation is slightly lower than the desorption result Eq. (66) and about five times larger than the absorption result given in Eq. (67). Now the exact temperatures of the absorption tests were not measured. When it is considered that the desorption liquid-gas interface may be at a lower temperature than the apparent one and vice versa for the absorption then the theoretical equation compares very favourably with the experimental results.

The effect of replacing the inert air phase by hydrogen is also accounted for by the modified theory, viz.,

$$K_G = 2\sqrt{\frac{2.3}{\pi . t_e}} = 1.71\ t_e^{0.5} \qquad (73)$$

Comparing with Eq. (68), and remembering that the theoretical values of D_G are lower than the practical ones, it is seen that agreement is good.

It would appear, then, that the penetration theory, applied to the gas phase, can predict a reasonable value for the mass transfer coefficient in cases where the bulk of resistance to transfer is found in the gas layers adjacent to the surface.

NOMENCLATURE for SECTION III

a, b, c, d = Constants

c = Concnetration of gas, lb.mols./ft^3.

c_e = Concentration of liquid in equilibrium with gas conc. c_e^*, lb.mols./ft^3.

c_e^* = Defined with c_e

c_o = Concentration of liquid in bulk, lb.mols./ft^3.

c_o^* = Concentration of gas in bulk, lb.mols./ft^3.

D_G = Diffusivity of gas, ft^2/hour.

D_j = Diameter of jet, ft.

D_L = Diffusivity of liquid, ft^2/hour.

F = Amount of gas absorbed up to time t_e, lb.mols/ft^2.

G = Gas flow rate, ft^3/hour.

H = Henry's Law constant, (lb.mols./ft^{3}gas)/(lb.mols/ft^{3}liquid)

K_G = Overall gas side coefficient, lb.mols./ft^2/hour/(lb.mols./ft^3)

K_L = Overall liquid side coefficient, lb.mols./ft^2/hour/(lb.mols./ft^3).

L_j = Jet length, ft.

N_a = Absorption or desorption rate, lb.mols./ft^2/hour.

R_e = Reynold's number, $\left(\frac{V_j D_j \rho}{\mu} \right)$

t = Time, hours.

t_e = Time of exposure, hours.

V_j = Jet velocity, ft./hour.

x = Depth of penetration, ft.

SECTION IV

INTRODUCTION

An attempt has been made to simulate the mechanism visualised by the penetration theory applied to high speed rotary absorbers. The conception of the mechanism assumes that, after a discontinuity, such as one of the rotor rings, or any other turbulence producer, a fresh surface of liquid is exposed to the gas. This surface absorbs gas at a rate given by the penetration theory for absorption into a stagnant liquid. Thus the fresh liquid surface exposed is assumed to be stagnant.

The technique employed utilises a stagnant liquid pool over which a gas chamber is passed at high speeds. This procedure is thought to dispose of any turbulence effects caused by liquid layer formation which may have been present in other workers' apparatus.[4,23,42] The technique suffers from the fact that the surface of the liquid pool is not fresh and thus some additional resistance to absorption may be apparent at the surface. It will be appreciated also that the time of contact of the liquid and the gas between rings in a rotary washer is very small, but it may be possible to obtain/

obtain times of contact of the same order as these.

The jet apparatus described elsewhere (see Section III) has given very short absorption times, but was in no way a stagnant liquid pool.

The apparatus was tested with the system ammonia-water in preference to carbon dioxide-water. The very small amounts of carbon dioxide which would be absorbed were considered too small for measurement.

DESCRIPTION OF ABSORBER

The liquid absorbent is contained in a socket 3.5 cm. x 3.5 cm. x .5 cm. deep, milled out of the top face of a bright steel bar 8 ft. x $2\frac{1}{4}$ ins. x 1 in. The socket is situated three feet from one end and is provided with a drain hole bored vertically through the bar. A plug for the drain fits into a recessed hole at the bottom of the socket. The approximate capacity of the socket is 6 cub.cms. The gas (solute) chambers are made from perspex in the form of boxes, see Fig. 48, $3\frac{1}{2}$, $6\frac{1}{2}$ and $12\frac{1}{2}$ ins. long. Preceding and coupled to any of the chambers is an 18 inch long gas chamber through which the liquid can be inserted via a stoppered hole into the socket. This permits

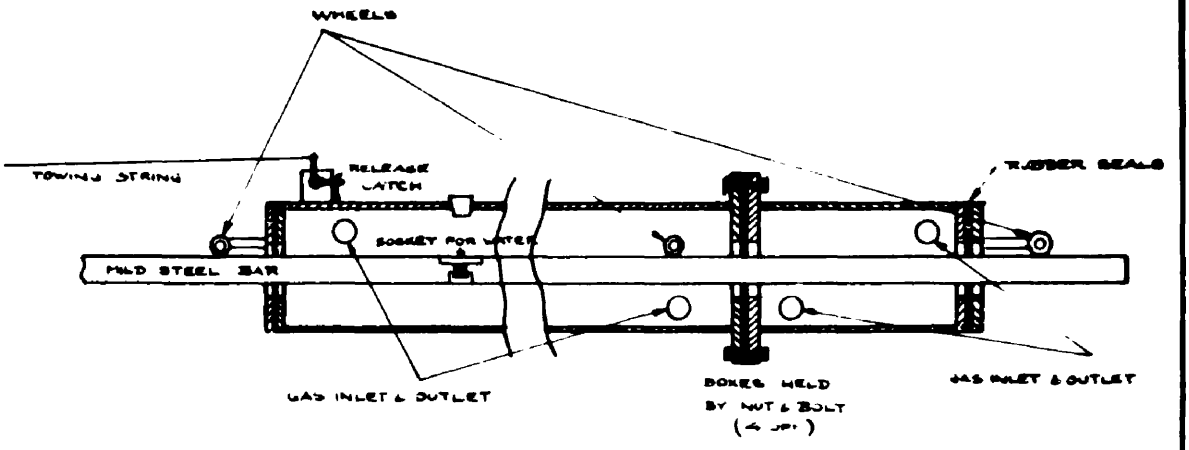


DIAGRAM of CHAMBERS

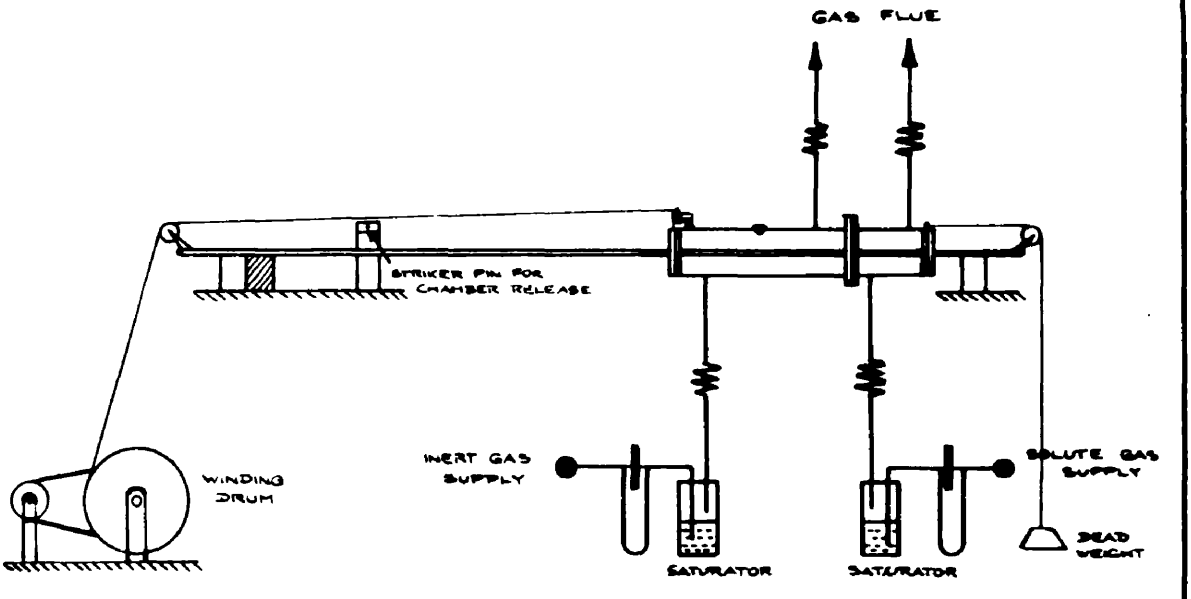


DIAGRAM of PLANT

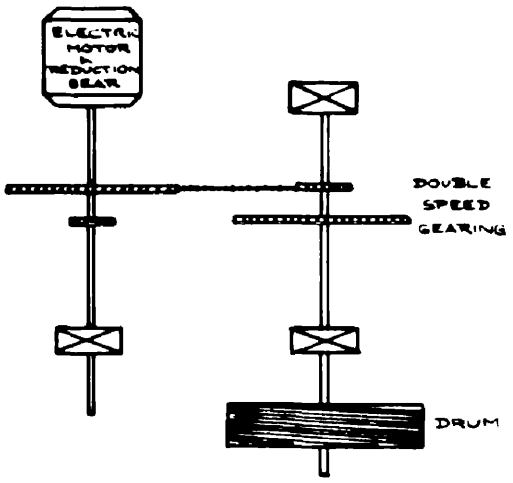
FIG. 48

the liquid to form a pool in the socket in the presence of any inert gas contained in the chamber. The two coupled chambers admit the bar through slots in the ends of the chambers and run on three pairs of ball raced wheels attached to axles at appropriate points along the chamber lengths. (Tightness is ensured by seals made from $^{1}/_{8}$ in. Gaco rubber inserted at the ends and at the join of the two chambers.) Each chamber has a gas inlet and gas outlet tube, their position dependent on the gas density relative to that of air for displacement purposes. The chambers are pulled over the socket at high speed by means of a cord winding onto a wooden drum driven by an electric motor. The drum is grooved in screw fashion to facilitate the winding of the cord. Different chain drive gears and drum diameters allow for speed variation which give an approximate range of exposure times of 0.01 - 10 seconds. The slower times of more than 0.5 seconds are assessed from the constant speed of the drum shaft, and the faster times, because they occur within the acceleration period of the drums (the length of the bar is limited), are recorded by a timing device operated by two contacts on the actual solute/

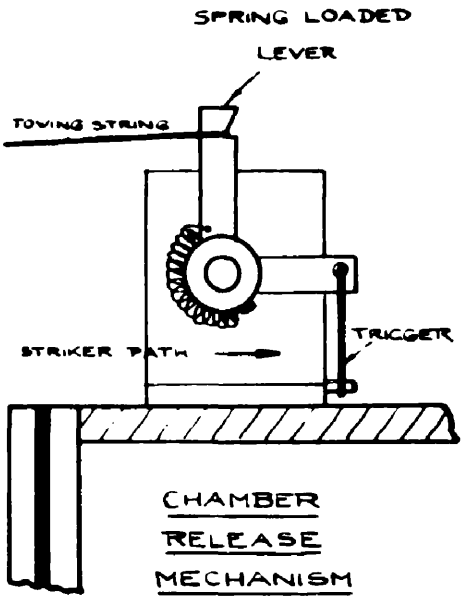
solute gas chamber.

The principle of this device can be seen in Fig. 49. A high constant speed (1425 r.p.m.) 1/4 H.P. electrical motor drives a wooden drum 2 ins. dia. and one foot long carrying a paper chart. The motor also drives, by chain gears, at half the input speed, a screwed rod along which a slide can travel. Mounted on this slide is a spring loaded marking device which records a constant pitch pencil trace on the paper chart. As the contacts on the moving solute gas chamber strike the marking device the pencil trace is disturbed. From the two disturbance marks an estimate of the contact time can be made to within 1/500 of a second. The only error incurred, apart from any slight variation in motor speed, is the distance travelled by the marker device between the two contact marks - but this is small compared with the length of the chambers (estimated error about 5% maximum at long contact times).

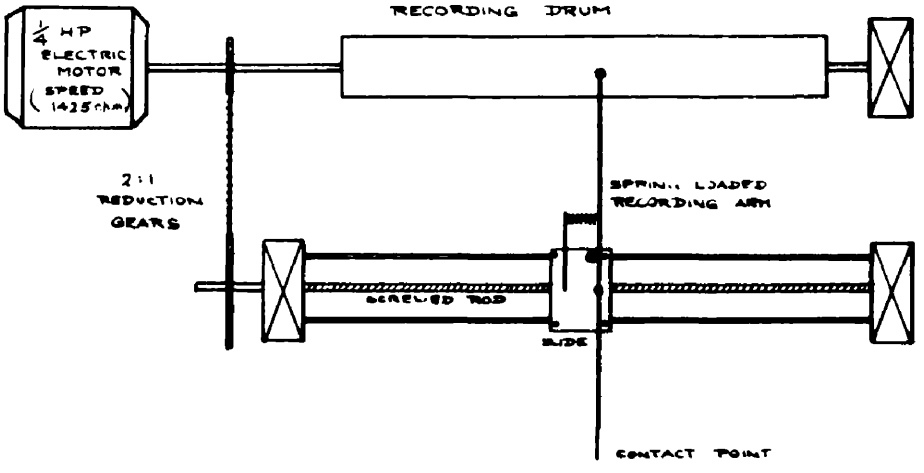
At the high speeds it is impossible for the chambers to decelerate quick enough within the length of bar available in the time interval after the switch controlling the electric drive motor has been turned off. Thus to prevent damage to the chambers a device is arranged/



WINDING DRUM MECHANISM



CHAMBER RELEASE MECHANISM



SHORT CONTACT TIME RECORDER

FIG. 49

arranged which disengages the towing cord at a point two feet from the end of the bar. Stopping time is determined by friction from the seals and any over run of the chambers is checked by a rubber cushion at the end of the bar.

EXPERIMENTAL

The absorber was tested using the system ammonia-water with air in the first chamber.

A four ml. sample of boiled distilled water was placed in the highly polished socket. A current of air (approximately 1 ft^3/hr.) was passed through the first chamber and ammonia gas from a gas cylinder fed through a water saturator into the second chamber at a rate of approximately 1 ft^3/hr. This balancing of flows reduced the chance of leakage of gases to either chamber. A delicate damp pH indicator paper inserted in the air chamber failed to detect any trace of ammonia. After the chambers have passed over the socket, the socket was emptied by removing the drain plug and thoroughly washed out with distilled water. Estimation of the ammonia content of the water sample was made by N/20 and N/100 sulphuric/

sulphuric acid using methyl red as indicator. End point determination at these low concentrations was excellent.

The first test runs were made in order to establish the effects of surface contamination by air in the time interval between filling of the socket and passage of the solute gas chamber over the socket. At first the results were irregular but this was partly due to uncertain concentrations of ammonia in the "solute" chamber. A filling time of five minutes for the $6\frac{1}{2}$ in. chamber was finally found to be adequate. It was also noted that sudden "swelling" of the liquid surface occurred when the ammonia chamber crossed the liquid pool. There was apparently a surface phenomena occurring either due to reduced surface tension or a heating effect which produced a change in the solid - gas - liquid miniscus. It was thought that this change, combined with the disturbance caused by uneven seal passage at the ends of the socket, was giving irregular results. To eliminate these effects a 0.2% solution of stergene in distilled water was substituted for the pure water and a smear of oil on the bar reduced a tendency for jerkiness in chamber travel/

travel. It was appreciated that the presence of this surface active agent would probably mean an extra resistance to mass transfer at the interface, but measurements with an oil film deliberately put onto the surface surface showed that any such effect would be small. The stergene in solution reduced the "swelling" effect to negligible proportions but did not appreciably lower the amount absorbed.

Results were now reasonably consistent and a series of test runs was then carried out to establish the effect of exposure time on absorption rates over the range .01 – 5 seconds.

RESULTS

Fig. 50 shows the effect of exposure time variation on absorption per unit area per cycle. It is evident that absorption results using different chamber lengths for the same exposure time are not compatible. The longer the chamber the greater the amount absorbed in the same time. It is possible to identify the sets of results for each chamber length by three distinct lines each with approximately the same gradient, viz.,

$$N_a = K.t_c^{0.51}$$

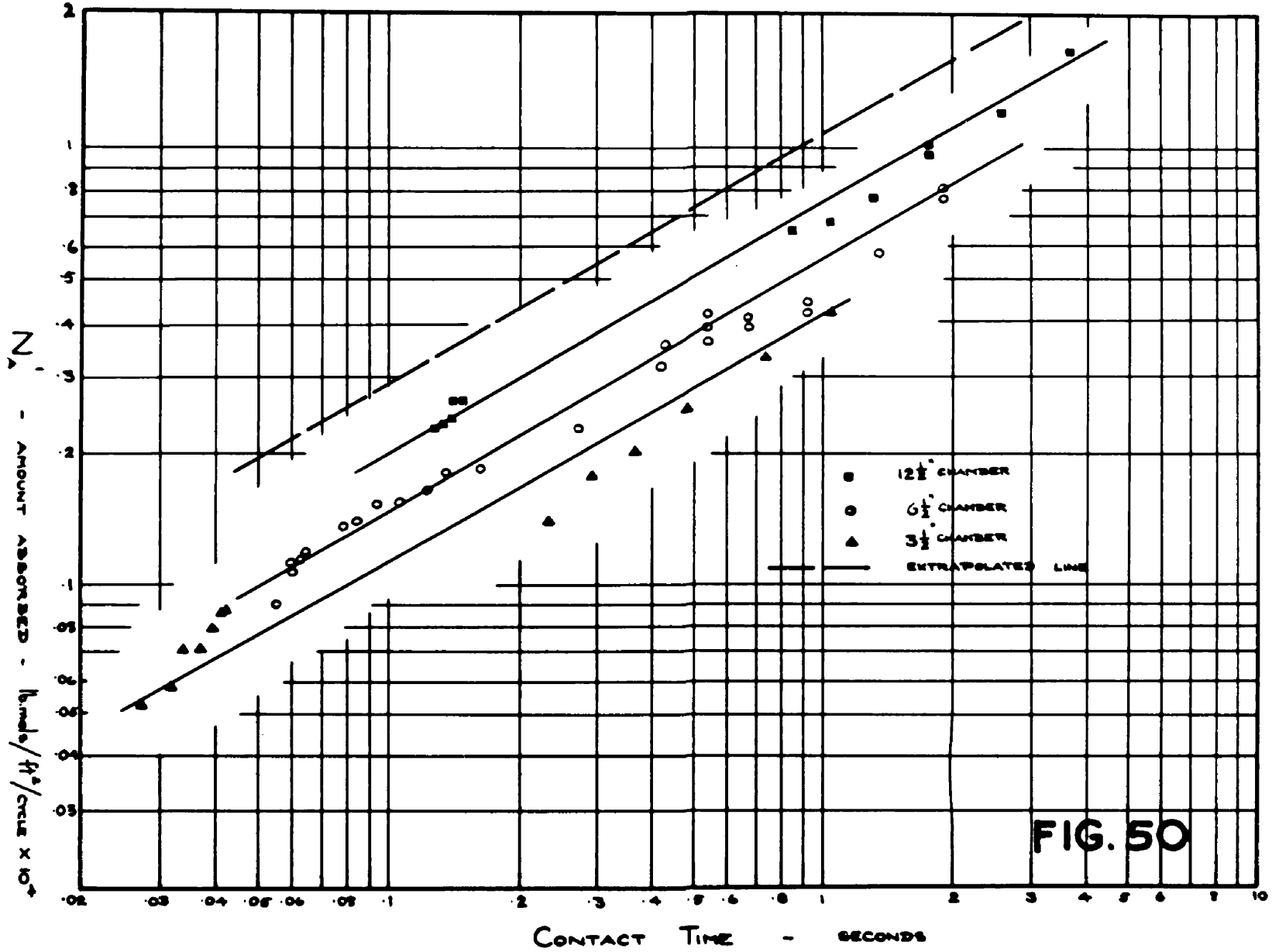

N_A - AMOUNT ABSORBED - lb.mols/ft²/CYCLE x 10⁴
CONTACT TIME - SECONDS
12½" CHAMBER
6½" CHAMBER
3½" CHAMBER
EXTRAPOLATED LINE

FIG. 50

DISCUSSION

The absorption of ammonia gas into water in this type of absorber will essentially be controlled by liquid film conditions as gas film resistance should be excluded by use of the pure gas. However, from the physical picture provided by the apparatus, a slight gas phase resistance may be present as there exists on the liquid surface a layer of air (or inert gas) which is not removed before the gas chamber crosses the socket. This layer is of the order of 1 m.m. thick for the series of results set out above. It is also probable that a second resistance to transfer will be present at the liquid surface, due (a) to adsorption of air molecules before the passage of the gas chamber and (b) to the presence of stergene molecules at the surface. Finally a notable effect on predicted values of absorption will arise from the increase in surface temperature, which for ammonia-water is of considerable magnitude. Thus it would appear that the rate of absorption as suggested by the Penetration Theory can show considerable divergency from actual results.

It is proposed, therefore, to consider the rate of/

of absorption as being controlled by the four resistances suggested, viz.,

1) Diffusional resistance due to air film.

2) Diffusional resistance due to adsorbed air and stergene.

3) Diffusional resistance in liquid.

4) Surface temperature effects.

The first resistance can be partly eliminated by mixing effects when the gas chamber wall passes over the socket. As the first seal on the solute gas chamber crosses a certain turbulence will be created in this air layer which, when combined with the inter-diffusion rate of air and ammonia gas, will substantially reduce any resistance due to the layer. The remaining effect will be partly nullified by the seal at the other end of the chamber. Here the layer will consist of ammonia and a certain interval of time will be required for the layer to diffuse into the atmosphere. Despite these considerations it has been noted that the different chamber lengths show discrepancies in absorption rates when an identical calculated contact time is considered. Such an end effect is most easily explained by the presence of this retained inert gas film. In the case of the largest chamber, to maintain/

maintain the same contact time as that of a shorter chamber, it has to travel faster. Then the coefficient of eddy diffusion for air and ammonia will be increased, which in turn causes the air layer to be removed in a shorter time interval and allows absorption to commence earlier in the contact time period. To eliminate these end effects, the absorption figures obtained in some specific exposure time have been plotted against the reciprocal of chamber length (Fig. 51). These curves have been extrapolated to give a figure for an infinite length of chamber, and can then give (Fig. 50) a final statement on absorption rate variation with time of contact - end effects eliminated. The relations link in linear and can be summarised in the form

$$N_a' = 0.000104\ t_c^{\cdot 51} \qquad (74)$$

The surface resistance due to absorbed air molecules and stergene molecules, has been shown to be negligible by the following experiments. The absorbed air molecules would probably show greater resistance to transfer of the ammonia if the preformed liquid pool

was/

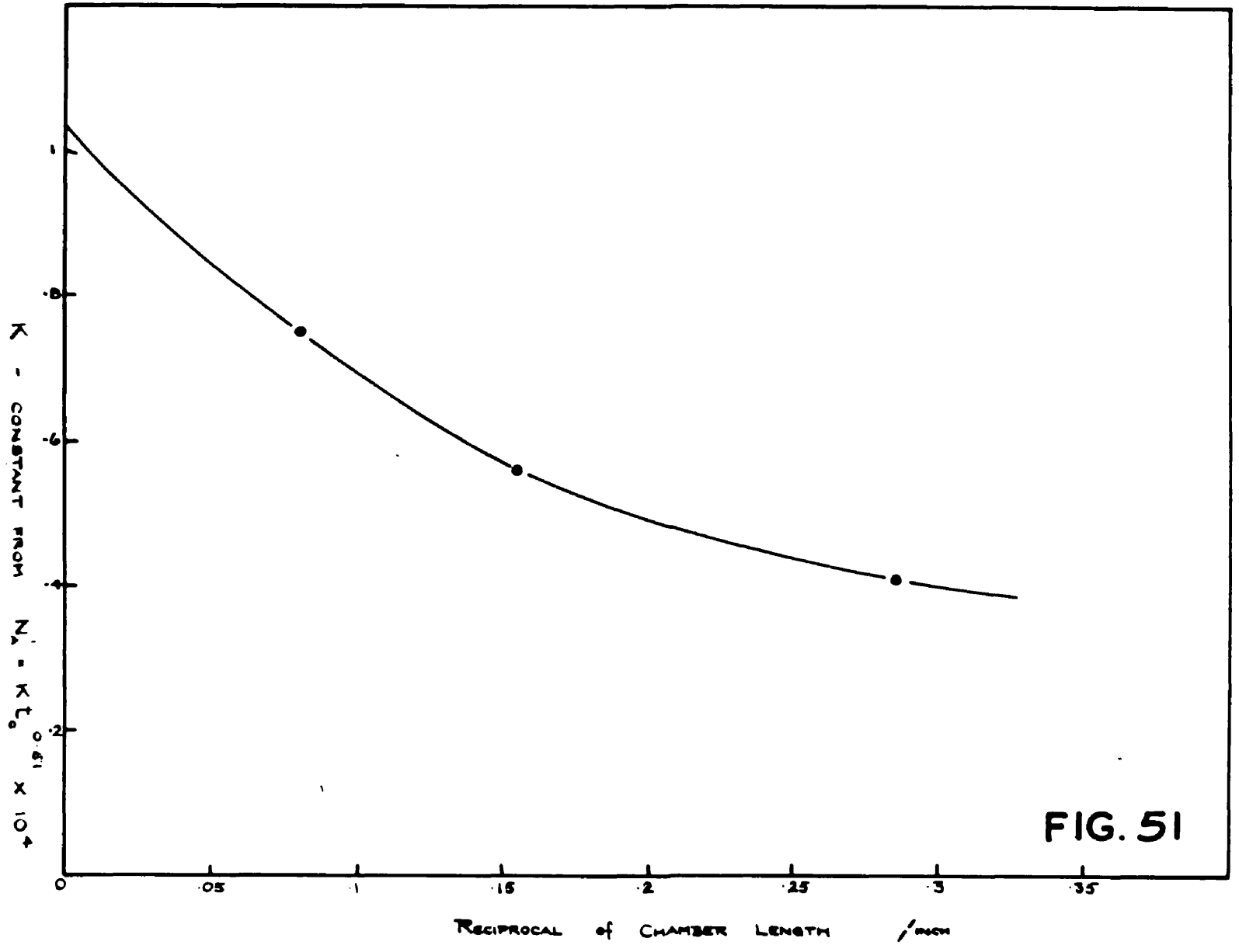

K - CONSTANT FROM $N_A = Kt_o^{0.61} \times 10^4$
1
·8
·6
·4
·2
0
·05
·1
·15
·2
·25
·3
·35
RECIPROCAL of CHAMBER LENGTH /'INCH

FIG. 51

was left for a long time in the socket before passage of the chamber, No such effect was shown over a time interval of one half hour as maximum. (It could possible be argued that at the instant of formation the surface of the liquid was very active, the adsorption was very rapid and further absorption during the succeeding time interval was negligible). The stergene molecules would undoubtedly migrate to the surface, but the consistency of results with and without stergene, apart from the occasional increase in absorption due to seal movement, showed that the stergene resistance was unimportant. These experiments, showing that the presence of "foreign" molecules at the surface was not a primary resistance factor in the ammonia-water absorption system, suggest that the molecules of air and stergene orientated themselves in the liquid molecule lattice at the surface in a way that allowed the ammonia molecules to pass through without interference.

Passing to liquid diffusion effects, the liquid side resistance in a system of this nature has been given by Higbie[4] and Danckwerts[23] as

$$N_a' = 2\, C_e \sqrt{\frac{D_L \cdot t_c}{\pi}} \qquad \text{——————} \qquad (75)$$

Now/

Now for the ammonia-water system at 15°C (average value of water initially in tests) c_e is given as 2.19 lb.mol./ft^3 [68] and D_L as 1.72 x 10^{-8} ft^2/sec.[68]

$$\therefore \quad N_a' = 0.000326\ t_c^{0.5} \qquad (76)$$

The extrapolated line from Fig. 50 has equation

$$N_a' = 0.000104\ t_c^{0.51} \qquad (74)$$

Thus comparing Eqs. (76) and (74) it is seen that the theoretical liquid film approach is about three times as large as the experimental result. The power indices of t_c are in very good agreement.

It is obvious that with such a reactive gas phase as 100% ammonia gas that there will be a large change in the temperature of the surface layer through which the molecules will diffuse. An estimate of the magnitude of this surface temperature rise can be made from a relationship given by Danckwerts[70]. Use of this data, which presumably does not hold for the extremely high temperatures encountered in ammonia absorption, gives a rise of the order of 35°C.

Thus, taking the temperature of the surface layers as/

as 50°C and amending the theoretical equation values for D_L and C_e to 4.08×10^{-8} $ft^2/sec.$[68] and 0.86 lb.mols./ft^3 [68] respectively, gives

$$N_a' = 0.000196\ t_c^{0.5} \qquad (77)$$

This result is in closer agreement with the experimental Eq. (74) but the discrepancy is still rather large. It is notable that if the system is considered on the basis of the gas film penetration concept, described in the previous section of this work, then the theoretical equation for absorption would be given by

$$N_a' = 2\, C_e^* \sqrt{\frac{D_V t_c}{\pi}}$$

$$= \frac{2}{359} \sqrt{\frac{0.24\ t_c}{10^3 \times \pi}}$$

$$\text{i.e. } N_a' = 0.000049\ t_c^{0.5} \qquad (78)$$

Eq. (78) suggests results which are about half the value of the experimental data.

Now the surface was not prepared in the absence of other gas (air) not is it certain that the small quantities/

quantities remaining at the surface during the transition from air to ammonia atmospheres were completely removed by relatively long contact. In such circumstances it is possible that an intermediate case of penetration, in which both media take part, has been set up. Time did not permit of the use of other gas (e.g. argon, hydrogen) as the inert medium for liquid surface formation, and it would appear that the matter is not yet determined.

NOMENCLATURE for SECTION IV

c_{e_*} = Saturation concentration in liquid, lb.mols./ft^3.
c_e^* = Concentration of 100% gas, lb.mols./ft^3.
D_L = Liquid diffusivity, ft^2/sec.
D_V = Gas diffusivity, ft^2/sec.
K = Constant
N_a' = Amount of gas absorbed, lb.mols./ft^2/cycle.
t_c = Contact time, secs.

SECTION V

In the first four sections of this work an attempt has been made to establish the actual mechanism of absorption (or desorption) of gas into (or from) a liquid by means of a comparison of the experimental data, obtained from various apparatus, with existing theories.

The bulk of evidence from the data suggests that the Whitman Two-film theory is inadequate from the point of view of dependence of mass transfer rates on the contact times of the phases, although a design precodure for estimating the volume of a transfer unit for rotary gas absorbers has been postulated on the basis of this two film theory. This practical application of a disputed theory has of course been widely followed elsewhere.

The dependence of mass transfer on contact time of phases suggests that either the Higbie-Danckwerts approach or Kishinevski's later theories will apply. Unfortunately the Higbie-Danckwerts analysis is limited to liquid-film control systems, as it appears to reduce to the "two-film" approach when applied to gas film controlled systems. A further drawback, in correlating/

correlating the data obtained in the rotary washer experiments with the theories of Danckwerts or Kishinevski was the difficulty in establishing the two parameters used in their approaches, viz., S, the rate of surface renewal, and D_t a combined eddy and molecular diffusion coefficient respectively.

However, from the results set out above it is obvious that some form of penetration theory must apply to gas film controlled absorption because of the variation in absorption or desorption rates with the phase contact time.

It is therefore proposed to develop a theory for the mechanism of all cases of gas absorption or desorption by means of an extension of Higbie's penetration theory.

Consider a system in which two immiscible fluids are brought into contact at a surface, $x = 0$, at a time $t = 0$. Suppose that a common component has concentrations c_1^o in fluid (1) and c_2^o in fluid (2). At $t = 0$, these concentrations are sensibly constant throughout each fluid.

As a result of contact, the component will move from one fluid to the other until equilibrium is established/

established finally at $t = t_\infty$. This equilibrium may be expressed as

$$c_1 = H.c_2 \qquad (79)$$

where H is some form of partition coefficient. In the particular case where fluid (1) is a gas and fluid (2) is a liquid, Eq. (79) is a form of Henry's Law. In the ideal case when H is constant for all the concentrations involved, $H.c_2$ may be regarded as the "effective concentration" in the liquid vis-a-vis the gas. Flow of the common component will be in the direction of lower effective concentration and will be continuous across the interface, with effective dynamic "equilibrium" between liquid and gas at this point.

A concentration gradient will therefore be established in each phase as soon as contact is made. When the time of contact is short, the component will diffuse into, or out of, each phase as if a semi-infinite fluid layer existed. Diffusion in a direction normal to the contact surface will follow the general equations set out below if relative motion of the surface layers in this short time is ignored.

$$\frac{\partial c_1}{\partial t} = D_1 \cdot \frac{\partial^2 c_1}{\partial t^2} \quad \& \quad \frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial t^2} \quad (80)$$

Here D_1 and D_2 are characteristic diffusion coefficients. At the actual interface, $x = 0$ and $c_1 = H.c_2$. The number of molecules entering (2) must equal the number leaving (1) or

$$D_1 \frac{\partial c_1}{\partial x} = D_2 \frac{\partial c_2}{\partial x} \quad \text{at} \quad x = 0 \text{ —— (81)}$$

Then the boundary conditions for Eqs. (80) become

$c_1 = c_1^o$	$x > 0$	$t = 0$:	$c_2 = c_2^o$	$x > 0$	$t = 0$
$c_1 = H.c_2$	$x = 0$	$t > 0$:	$c_2 = H.c_2$	$x = 0$	$t > 0$
$c_1 = c_1^o$	$x = 0$	$t < 0$:	$c_2 = c_2^o$	$x = 0$	$t < 0$

Then integration of Eqs. (80) to give c in terms of x show

$$c_1 = c_1^o + A \operatorname{erfc} \frac{x}{2\sqrt{D_1 t}} \text{ ——— (82)}$$

$$c_2 = c_2^o + B \operatorname{erfc} \frac{-x}{2\sqrt{D_2 t}} \text{ ——— (83)}$$

Here $$A = \frac{\sqrt{D_2}}{\sqrt{D_2} + H\sqrt{D_1}} \cdot (H.c_2^o - c_1^o)$$

and $$B = \frac{\sqrt{D_1}}{\sqrt{D_2} + H\sqrt{D_1}} \cdot (c_1^o - H.c_2^o)$$

Now/

Now the flux of molecules from (2) to (1) is

$D_1 \cdot \frac{\partial c_1}{\partial x}$ at $x = 0$. But from Eq. (82)

$$D_1 \frac{\partial c_1}{\partial x} = - A \cdot \frac{D_1}{\sqrt{\pi D_1 t}}$$

Substituting for A

$$- A \cdot \frac{D_1}{\sqrt{\pi D_1 t}} = \frac{\sqrt{D_2}}{\sqrt{D_2} + H\sqrt{D_1}} (c_1^{o} - H.c_2^{o}) \sqrt{\frac{D_1}{\pi t}}$$

Then the average flux of molecules from $t = 0$ to $t = t_e$ will be

$$\frac{1}{t_e} \int_{o}^{t_e} \frac{\sqrt{D_2}}{\sqrt{D_2} + H\sqrt{D_1}} (c_1^{o} - H.c_2^{o}) \sqrt{\frac{D_1}{\pi t}} \cdot dt$$

$$= 2 \frac{\sqrt{D_2}}{\sqrt{D_2} + H\sqrt{D_1}} (c_1^{o} - H.c_2^{o}) \sqrt{\frac{D_1}{\pi t_e}} \quad \text{——} \quad (84)$$

Now

$$\frac{\sqrt{D_2}}{\sqrt{D_2} + H\sqrt{D_1}} \equiv \frac{1}{1 + H\sqrt{\frac{D_1}{D_2}}}$$

and when $H\sqrt{\frac{D_1}{D_2}} \ll 1$

Eq. (84) reduces to

$$N_a(\text{the average flux}) = 2(c_1^{o} - H.c_2^{o}) \sqrt{\frac{D_1}{\pi t_e}} \quad -(85)$$

This/

This equation suggests that all control of mass transfer is vested in conditions of Phase I, whatever this fluid may be.

Thus for the system air (1) - water (2) with ammonia as the common component D_1 is 0.886 and D_2 is 6.8×10^{-5}. The value of H is not constant, but for partial ammonia pressure of 0.1 atm. approximates to 6.6×10^{-4} with water at 20°C. (All data in lb.ft.hr. systems)

$$H\sqrt{\frac{D_1}{D_2}} = .074$$

and gas phase conditions will control in accordance with Eq. (85).

Again when $H\sqrt{\frac{D_1}{D_2}} \gg 1$ Eq. (84) becomes

$$N_a = 2H\sqrt{\frac{D_2}{D_1}}\,(c^o - H.c^o)\sqrt{\frac{D_1}{\pi t_e}}$$

which reduces to

$$N_a = 2\left(\frac{c_1}{H} - c_2^{\,o}\right)\sqrt{\frac{D_2}{\pi t_e}} \qquad \text{(86)}$$

Now this expression for rate of mass transfer relates all flow to the conditions of fluid (2).

For air (1) and water(2) as before, but with carbon dioxide as the common component, D_1 is 0.535, and D_2 is $.58 \times 10^{-4}$. H is again not constant/

constant, but for carbon dioxide a partial pressure of 0.1 atm, the value at 20°C is about 1.14. (All data, as before, in ft.lb.hr. units.)

Then

$$H\sqrt{\frac{D_1}{D_2}} = 110$$

and liquid film conditions will control in accordance with Eq. (86). Eq. (86) is identical with the expression derived by Higbie and closely resembles the Danckwerts model.

Now consider conditions at the interface where

$$c_1^{\,i} = c_1^{\,o} + A \operatorname{erfc} \frac{+x}{2\sqrt{D_2 t}}$$

and $x = 0$ whence,

$$\operatorname{erfc} \frac{x}{2\sqrt{D_2 t}} = 1$$

Then

$$c_1^{\,i} = c_1^{\,o} + A$$

$$= c_1^{\,o} + \frac{\sqrt{D_2}}{\sqrt{D_2} + H\sqrt{D_1}} (H.c_2^{\,o} - c_1^{\,o})$$

$$= \frac{H\,(c_1^{\,o}\sqrt{D_1} + c_2^{\,o}\sqrt{D_2})}{\sqrt{D_2} + H\sqrt{D_1}}$$

This expression is independent of time (for short contact time) and suggests that a fluid interfacial concentration intermediate between $c_1^{\,o}$ and $H.c_2^{\,o}$/

$H.c_2^o$ is immediately established as interfacial contact occurs.

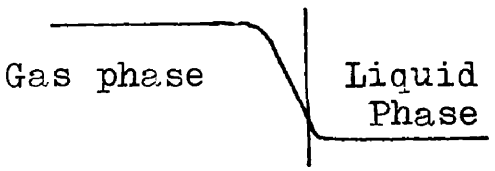
In the typical systems where (1) ammonia and (2) carbon dioxide are being absorbed by solute free water ($c_2^o = 0$) these interfacial concentrations in the gas phase reduce to

a) NH_3 $\quad c_1^i = 0.066\ c_1^i$

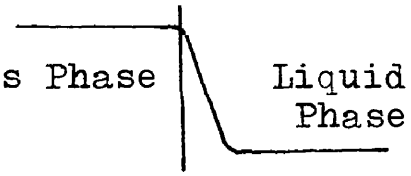
b) CO_2 $\quad c_1^i = 0.99\ c_1^o$

It is clear that these two can be represented as

a)



b)



or the penetration theory, applied to both gas and liquid phases, has produced a picture of interfacial conditions which is identical with that of the "two film" hypothesis.

Now the work of Higbie, Danckwerts, Lynn and others has established the penetration theory for sparingly soluble gases and the conditions shown in case (b) above. The present work on jet absorption - desorption, and particularly the latter, certainly supports the penetration theory, as developed here, in case (a).

At this point a return may be made to Section I, Table/

Table V, which is summarised below.

	$K_G a$ (exprtl.)	Higbie - Danckwerts	Sherwood - Goodgame	X
Methanol-Water	535	5250	920	830
Ammonia-Water	545	1400	660	1280
Acetone-Water	468	460	370	510
Methyl Acetate -Water	300	170	190	400
Carbon Dioxide -Water	0.77	0.77	0.77	0.77

It will be seen that the Higbie-Danckwerts approach does not give a satisfactory explanation of the experimental results. The best agreement between theory and practice is given by the Sherwood-Goodgame formula, as set out in Eq. (56a).

If now Eq. (84) is applied in all cases, as shown in Column X with calculated results based on carbon dioxide as before, then the figures, while wide of the mark for ammonia and methyl acetate, are in the right order and perhaps not so far from actual experiment when possible causes for discrepancy are noted.

In particular, it does appear that ammonia in absorption tends to establish a dynamic equilibrium with/

with high surface concentration thus reducing the actual rate below that which might be calculated from a knowledge of steady gas and liquid concentrations. This point has been further developed in a paper submitted to Chemical Engineering Science jointly with Dr. F. Rumford.

Passing now to the travelling chamber experiments (Section IV) it will be recalled that a final experimental correlation gives the amount absorbed as

$$F = 0.000104\ t_e^{0.51}$$

Calculation on the basis of Higbie's formula, where t_e was the period of absorption based on liquid conditions, suggested a value of 0.0003 for the constant ($F = 0.0003\ t_e^{0.5}$), or if a somewhat sweeping assumption is made for temperature change 0.0002. On the other hand calculation on the basis of diffusion in an inert gas phase following Eq. (85) gave much lower results and a value for the constant of 0.00005.

It is certain that insufficient inert gas was present to justify the use of Eq. (85), and in these circumstances/

circumstances all that can be done is to note the modifying influence of the inert gas. The experimental result, lying between that which could be expected were only liquid involved, and that which could be calculated on the basis of gas diffusion by the penetration hypothesis, thus supports the general form of penetration theory which has been derived.

A paper[71] which has just come to hand suggests that both static film and penetration effects are always present in any mass transfer problem. They propose a "film penetration" model with "young" and "old" elements of surface and a balance between these two set by the Schmidt Number of the system. For high Schmidt Numbers mass transfer follows a penetration theory, and for low Number values steady film conditions are set up. However, this analysis deals only with penetration into one fluid phase and its application to the two fluid systems studied in the present work has not been considered.

NOMENCLATURE for SECTION V

A, B } Integration constants.

c = Concentration, lb.mols./ft^3.

c_1 = Concentration of common component in fluid (1) after time t, lb.mols./ft^3.

c_1^o = Concentration of common component in fluid (1) at time t = 0, lb.mols./ft^3.

c_1^i = Concentration of common component in fluid (1) at interface, lb.mols./ft^3.

c_2 = Concentration of common component in fluid (2) after time t, lb.mols./ft^3.

c_2^o = Concentration of common component in fluid (2) at time t = 0, lb.mols./ft^3.

D_1 = Diffusivity of common component in fluid (1), ft^2/hour.

D_2 = Diffusivity of common component in fluid (2), ft^2/hour.

H = Henry's Law Constant (or Partition Coefficient) = c_1/c_2

N_a = Average flux of molecules, lb.moles/ft^3/hour.

$K_g a$ = Overall gas film coefficient, lb.moles/ft^3/hour/atm.

t = Time, hours.

t_e = Time of contact of phases, hours.

x = Distance from common interface, measured normal to surface, feet.

GENERAL CONCLUSIONS AND SUGGESTIONS FOR DEVELOPMENT

The first conclusion that can be drawn from all sections of the present work is that mass transfer between a gas and a liquid phase appears to follow some form of "penetration" theory, rather than one of diffusion through relatively stagnant interfacial films. The introduction of both fluid phases into the general penetration theory initiated by Higbie has explained in reasonable terms a number of experimental results. There is also a marked similarity between the concentration system predicted by this two fluid penetration hypothesis and that suggested by the Whitman film theory. The success of this latter theory in correlating experimental results may be bound up in this similarity.

The second conclusion may be briefly summarised in the table set out on page 69 where values for H, a Henry's Law constant, vary from 408 to 0.049 but only give one value notably above unity - carbon dioxide at 408. Now a full analysis, especially in view of novel developments in the penetration hypothesis, waits upon the use of a range of substances having values of

e.g./

e.g. 100, 50 and 10. It is not easy to hit upon suitable gas-liquid systems having these characteristics. Attempts should be made to broaden the field by introduction of non aqueous solvents, using perhaps low boiling organic liquids in the gas phase.

The work described in this thesis stemmed from an attempt to develop a high efficiency gas scrubber giving high absorption rates in a small scrubbing volume. It is for this reason that so much of the earlier sections is devoted to actual working details of such scrubbers and to analysis of their operation. Perhaps it is only necessary here to point out that such units are based theoretically upon the need to produce fresh interface rather than high turbulence, although the two desiderata may be intimately connected. It is towards the distinction between turbulence and surface renewal that further work might well be directed and perhaps the paper by Toor and Marchello, referred to above,[71] may be a useful pointer in this direction. The importance of widening the field of fluids investigated would again be a vital part of such work, and it is perhaps with reiteration of this recommendation that the thesis is concluded.

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